University of Alberta

Degradation and Rates of Reaction of Estrone in an Ozone/Hydrogen Peroxide Batch Treatment System

By

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Abstract

Ozone/hydrogen peroxide batch treatment was utilized for the degradation of the steroidal hormone estrone. The competitive kinetics method was used to determine the rates of reaction for direct ozone and estrone (E1), and for hydroxyl radicals and estrone. Experiments were performed at three pH levels (4, 7, and 8.5) and at three different molar O_3/H_2O_2 ratios (1:2, 2:1, and 4:1), all at temperatures averaging 20°C.

It was found for the direct ozone-E1 reaction that rate constants ranged between 3.65×10^3 $M^{-1}s^{-1}$ at pH 4, O_3/H_2O_2 = 1:2, and 2.32×10^7 $M^{-1}s^{-1}$ at pH 8.5, O_3/H_2O_2 = 2:1. By far, pH had the greatest influence on rate reaction, whereas O_3/H_2O_2 ratio was found to be slightly statistically significant.

For the hydroxyl radical-E1 reaction, apparent rate constants ranged between 1.14×10^{10} $M^{-1}s^{-1}$ at pH 7, O_3/H_2O_2 = 2:1, and 7.03×10^{10} $M^{-1}s^{-1}$ at pH 4, O_3/H_2O_2 = 2:1. Again, pH was statistically significant but O_3/H_2O_2 ratio was not. The regression output for this group of experiments showed considerable noise and the possibility of an unknown regressor.

Overall, O_3/H_2O_2 is shown to be an effective treatment for E1. It was found that pH is a statistically significant experimental factor and is more significant to direct ozone reactions than to hydroxyl radical reactions. The role of O_3/H_2O_2 ratio in rate reactions is still unclear at this time.

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List of Symbols, Nomenclature, or Abbreviations

ANOVA	Analysis of variance
AOP	Advanced oxidation process
DOM	Dissolved organic matter
DS	Downstream of
DW	Drinking water
E1	Estrone
E2	17β-estradiol
E3	Estriol
EDC(s)	Endocrine disrupting chemical(s)
eEDC(s)	Estrogenic endocrine disrupting chemical(s)
EE2	17α-ethinylestradiol (also ethynylestradiol)
HPLC	High performance liquid chromatography
HRT	Hydraulic retention time
H_2O_2	Hydrogen peroxide
$k_{O3\text{-}E1}$	Rate constant for reaction of ozone with contaminant
O_3	Ozone
PAC	Powdered activated carbon
p-CBA	*p*-chlorobenzoic acid
R	River
SRT	Sludge retention time
SW	Surface water
TBA	Tert-butyl alcohol
TiO_2	Titanium dioxide
US	Upstream of
UV	Ultraviolet radiation
WTP	Water treatment plant
WWTP	Wastewater treatment plants
YES	yeast estrogen screen

1. Introduction

The increasing sophistication of environmental chemistry has led to further differentiation of environmental contaminants. Classes of contaminants are being subdivided to allow for more depth of research into particularly harmful, widespread, or recalcitrant subclasses.

One contaminant class of interest is endocrine disrupting compounds (EDCs), and it has a well-known subclass referred to as estrogenic EDCs (eEDCs). Endocrine disrupting compounds are defined as "chemicals that interfere with the synthesis, secretion, transport, binding, action or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development and or behavior" (EPA, 1997). Exposure to EDCs could therefore potentially have a substantial effect on the body, disrupting bodily function and processes, growth and development, and potentially cause or accelerate diseases such as cancer. Estrogenic EDCs are so named because they mimic or block natural estrogen (Snyder et al. 2003).

Estrogenic EDCs may be surfactants, plasticizers or hormones, and some of the most notable eEDCs are the steroidal hormones estrone (E1), 17β-estradiol (E2), estriol (E3) and the synthetic hormone 17α-ethinylestradiol (EE2). Various treatments have been studied for the removal of eEDCs from water and wastewater, including membrane filtration, biological treatment, chemical oxidation treatment and advanced oxidation processes (AOPs). In terms of AOPs, both catalytic (i.e. use of solid catalysts) and homogeneous treatment processes have been studied.

Advanced oxidation processes (AOPs) are characterized by the generation of hydroxyl radicals and have been investigated for the treatment of eEDCs. Studies to date have looked at the use of ozone, UV, and UV/H_2O_2 to degrade various hormone eEDCs (Huber et al., 2003; Rosenfeldt and Linden, 2004; Lin and Reinhard, 2005). These studies have demonstrated that the above-mentioned processes show promise in treating hormone eEDCs, with ozone in particular being quite effective. Of the estrogenic hormones, E2 and EE2 seem to be the most extensively studied, while E1 and E3 much less so. This is in spite of the extensive environmental presence demonstrated for E1 (Kuch and Ballschmiter, 2001; Kolpin et al., 2002; Benijts et al., 2004).

To date, O_3/H_2O_2 treatment has been little investigated for any of the target contaminants. There are numerous reasons why O_3/H_2O_2 treatment would be a good candidate for further investigation. First and foremost, it remains to be seen whether H_2O_2 would affect the decomposition of ozone in a treatment setting. It may prove to be complementary to direct ozone reaction or facilitate increased hydroxyl radical reaction. Experimentation is necessary to determine this. Second, combined direct ozone-hydroxyl radical treatment may prove to be more beneficial overall, due to its dual oxidation mechanisms. Third, because of the unstable nature of its oxidants, O_3/H_2O_2

treatment is quite unlikely to leave any oxidant residual, and does not require the use of expensive catalysts such as Fenton's reagent requiring removal after treatment. E1 is an excellent contaminant candidate, because, as mentioned above, it has received less research attention than some of the other estrogenic hormones in spite of its environmental relevance.

For these reasons, O_3/H_2O_2 treatment in a batch process was investigated for the degradation of estrone (E1). The objectives of this work were to:

- report the current state of knowledge regarding water and wastewater levels of the steroidal hormones E1, E2, E3 and EE2, as well as their fate and behaviour in treatment plants and various treatment technologies, with particular focus on ozonation and AOP technologies;
- determine rate constants for the reaction between direct ozone and E1 (Part I), and between hydroxyl radicals and E1 (Part II) (for three different pH levels and three different molar O_3/H_2O_2 ratios); and
- determine the statistical significance of both pH and O_3/H_2O_2 ratio to the rates of reaction of E1 and the oxidants used.

2. Literature review

Endocrine disrupting compounds may be pesticides, pharmaceuticals, plasticizers, surfactants, industrial compounds, human hormones excreted into wastewater, or naturally occurring plant and fungal-derived hormones, to name several. A few examples of known EDCs may be seen in Table 1.

As seen in Table 1, EDCs may be found among various chemical classes and sources. It should be noted that Table 1 only presents a very limited list of known EDCs, for the sake of brevity. It should also be noted that of the 14 EDCs presented in Table 1, over half (eight) are estrogenic. This demonstrates that estrogenic EDCs account for the majority of EDCs. Estrogenic EDCs have been demonstrated to be widely prevalent in aquatic environments and present in higher concentrations than other EDCs (Kolpin et al., 2002, Laganà et al., 2004 among others).

Table 1. Selected EDCs and their sources

Chemical name	Mode of action
Industrial	
Bisphenol A[1]	Estrogenic[3]
Alkylphenols (from C5 to C9)[1]	Estrogenic[3]
Phthalates (butylbenzyl, di-(2-ethylhexyl), di-*n*-butyl)[1,2]	Estrogenic[4]
By-product of waste incineration	
Dioxins[2]	Estrogenic[4]
Polychlorinated dibenzofurans[2]	Estrogenic[3]
Benzo(a)pyrene[1]	Androgenic[3]
Hormones (natural, synthetic, or identical to natural hormone)	
Estradiol 17β and its ester-like derivatives[2]	Estrogenic[4]
Progesterone[2]	Estrogenic*
Testosterone[2]	Androgenic**
Pesticides	
Atrazine[2]	Affects neuroendocrine-pituitary systems, testosterone metabolism[3]
Chlordane (cis- and trans-)[2]	Affects testosterone and progesterone activity[3]
Endosulfan[2]	Estrogenic[3]
Malathion[2]	Thyroid[3]
Vinclozolin[2]	Androgenic[3]

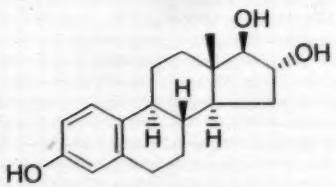
Note: *Progesterone is here classified as estrogenic because it is a female sex hormone – it may not necessarily have the same effects or mode of action as conventional estrogens (RSC 1999). **Testosterone is classified as androgenic (RSC, 1999)

1. NIES, 2004 2. COEC, 2001 3. OSF, 2007 4. Richardson, 2003

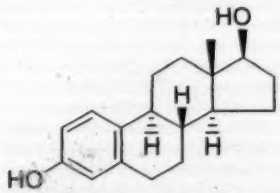
Wildlife surveys have partly substantiated concerns regarding eEDC presence in the environment. One of the most well-known surveys showed high incidence of intersex in fish living downstream from wastewater treatment plants (WWTPs) (Jobling et al., 1998). The eEDC presence in aquatic environments is notable because it is thought that water (both surface water and ground water) as well as treated wastewater represent both the most affected environmental media, and the most significant human exposure pathways in regards to EDCs (Daughton and Ternes, 1999). As a result, many are concerned that eEDC exposure may have adverse effects on human and environmental health. As such, it is important to understand and reduce EDC levels in the environment.

Of the eEDCs, steroidal estrogen hormones such as estrone (E1), 17β-estradiol (E2), estriol (E3) and the synthetic hormone 17α-ethinylestradiol (EE2) have been demonstrated to constitute a strong majority of the estrogenicity burden of municipal wastewater (Desbrow et al., 1998, Routledge et al., 1998, Aerni et al., 2004, Servos et al., 2005, and others). As

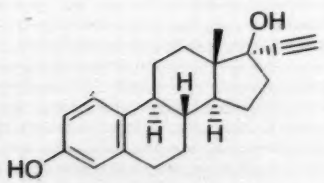
such, steroidal estrogens may be considered to be the most significant EDCs with regards to human and environmental health risks. This puts the impetus on water and wastewater utilities to reduce the levels of these EDCs in their effluents. Structures for these steroid hormones may be seen in Figure 1.



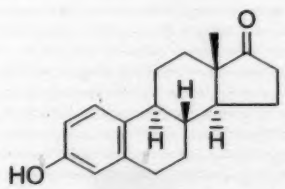
Estrone (E1)



17β-Estradiol (E2)



17α-Ethinylestradiol (EE2)



Estriol (E3)

Figure 1. Structures of prevalent estrogens E1, E2, EE2 and E3.

EDC occurrence in water

As water is one of the most important exposure pathways for EDCs, it is important to determine the level of contamination in this medium. Numerous studies have looked at the presence of pharmaceuticals and EDCs in water. In one study, the US Geological Survey conducted a comprehensive survey of American water bodies, in which estrogens were found at frequencies ranging from 5.7% to 21.4%, demonstrating that estrogenic hormones can be considered to be fairly wide-spread (Kolpin et al 2002). Median concentrations ranged from 0.009 μg/L to 0.16 μg/L. A summary of several additional studies pertaining to the environmental levels of estrogenic hormones may be seen in Table 2. Single values represent a reported average.

Table 2. Occurrence of estrogenic EDCs in the environment

Hormone	Sampling location	Concentration range (ng/L)
Estrone (E1)	a. Belgian rivers[1] b. German WTP; DW; rivers and DW[2,3] c. Tiber R., Italy[3] d. DS, US French WWTPs; French SW[4]	a. 21.7 b. 0.16; 0.70, 0.40 c. l. 5 - 12 d. 2.2 – 3; 1.1, 1.2; 1.4, 1.8
17β-estradiol (E2)	e. Tiber R., Italy[5] f. German rivers, DW[3] g. Nevada SW[6] h. DS, US French WWTPs; French SW[4]	e. 2 – 5 f. 0.60, 0.70 g. < 1.0 h. 3.0 – 3.2; 1.4, 2.1; 1.7, 1.8
17α-ethinylestradiol (EE2)	i. Tiber R., Italy[5] j. German rivers, DW[3] k. Nevada SW[6] l. DS, US French WWTPs; French SW[4]	i. N.D. – 1 j. 0.80, 0.35 k. 3.6 – 14 l. 1.8 – 2.9; 1.1, 1.5; 1.3, 1.4
Estriol (E3)	m. Tiber R., Italy[5] n. DS, US French WWTPS; French SW[4]	m. 2 – 6 n. 2.1, 2.5; 1.0, 1.5; 1.8, 2.2

Note: R: river; SW: surface water; DW: drinking water; WTP: water treatment plant; WWTPs: wastewater treatment plants; DS: downstream of; US: upstream of

1. Benijts et al., 2004; 2. Verstraeten et al., 2003; 3. Kuch and Ballschmiter, 2001; 4. Cargouët et al., 2004; 5. Laganà et al., 2004; 6. Vanderford et al., 2003.

As seen in Table 2, eEDCs have been detected in both surface water and drinking water. With regards to surface water, Table 1 shows that higher levels of eEDCs can be found downstream of wastewater treatment plants than upstream, demonstrating the contribution of wastewater treatment plants to eEDC contamination. An eEDC presence in drinking water is also shown, although whether the levels seen (< 1 ng/L) are a threat to human health is uncertain (Verstraeten et al., 2003; Kuch and Ballschmiter, 2001). It is also worth noting that in the instances where hormones were detected in drinking water, the concentrations were within the same order of magnitude as the hormone concentrations in surface water. This suggests that while some measure of EDC removal is occurring in WTPs, it is not sufficient to completely remove EDCs.

EDC occurrence in wastewater

While potential EDC contamination of drinking water garners much of the attention regarding EDCs, wastewater is an important aspect of the issue because wastewater has been implicated as a source of EDCs in water bodies and ultimately drinking water supplies. Table 3 shows a summary of selected EDC concentrations in WWTP influent and effluents.

Table 3. eEDC Concentrations in various WWTP influents and effluents

Chemical	Concentration (µg/L)	Influent or Effluent	WWTP Location(s)
Estrone (E1)	a. 0.188[1] b. 0.020 – 0.075[2] c. 0.001 – 0.1[2] d. 0.0096 – 0.0176[3] e. 0.0043 – 0.0072[3]	a. Influent b. Influent c. Effluent d. Influent e. Effluent	a. Berlin-Ruhleben, Germany b, c. across Canada d, e. Paris area, France
17-estradiol (E2)	f. 0.0118[1] g. 0.0025 – 0.025[2] h. 0.0005 – 0.015[2] i. 0.0111 – 0.0174[3] j. 0.0045 – 0.0086[3]	f. Influent g. Influent h. Effluent i. Influent j. Effluent	f. Berlin-Ruhleben, Germany g, h. across Canada i, j. Paris area, France
17-ethinylestradiol (EE2)	k. 0.0088[1] l. 0.0049 – 0.0071[3] m. 0.0027 – 0.0045[3]	k. Influent l. Influent m. Effluent	k. Berlin-Ruhleben, Germany l, m. Paris area, France

Note: 1. Verstraeten et al., 2003; 2. Servos et al., 2005: 3. Cargouët et al., 2004.

As shown in Table 3, concentrations for the same EDC can vary by an order of magnitude or more. This could make developing treatment systems for EDCs very difficult, as there may be wide concentration ranges to contend with in addition to the many different EDCs.

Numerous groups of researchers have surveyed effluent estrogenicity as well as eEDC concentrations. One group of researchers examined influent and effluent estrogenicity in 18 Canadian wastewater treatment plants, using the yeast estrogen screening (YES) bioassay (Servos et al., 2005). It was found that influent estrogenicity ranged from not detectable to 148% response, with a mean of 79% response. Percent response may refer to percent difference between a control and the sample, but this is uncertain as percent response was not defined in the paper. Effluent estrogenicity ranged from not detectable to 110%

response, with a mean of 50.2% response. Effluent estrogenicity exceeded influent estrogenicity in four plants. For three of those plants, effluent E1 concentrations exceeded influent, and two of those plants also showed higher E2 concentration in effluent than in influent. This suggests the possibility of hormonally active intermediates resulting from partial degradation of eEDCs, or the possibility of cleavage of conjugated forms of the hormone of interest. It is also possible that non-hormone eEDCs (i.e. bisphenol A, alkylphenols) contributed to estrogenicity and were not degraded to the same extent that the hormonal eEDCs were.

Another groups of researchers examined decreases in French wastewater estrogenicity due to treatment, via use of the MCF-7 breast cancer cell assay (Cargouët et al., 2004). Estrogenicity declined between 62% and 92% between intake and discharge, for four wastewater treatment plants. Hormone concentrations decreased by 44% to 59% for E1, 43% to 60% for E2, 40% to 67% for E3 and decreased between 34% and 45% for EE2, in the aforementioned treatment plants.

Fate and behaviour of EDCs during water and wastewater treatment

Most would acknowledge that the fate and behaviour of EDCs during treatment is in large part determined by the characteristics of the EDCs themselves. Parameters such as water solubility, octanol-water partitioning and sorption would be considered to dominate contaminant fate. That being said, at the extremely low overall concentrations that EDCs occur at, conventional parameters may be of uncertain impact. For instance, many hormones are considered insoluble in water; however, it is unlikely that solubility limits were tested in the range of micrograms and nanograms per litre.

Thus, conventional parameters may have limited accuracy in predicting the fate and behaviour of EDCs in treatment processes. Mass balances, on the other hand, offer a more reliable idea of what happens in treatment processes. As this paper deals with wastewater management as opposed to solids management, fate of EDCs within the solids stream shall not be discussed in detail.

EDC fate observational studies

A number of observational studies have examined the fate of EDCs during water and wastewater treatment. One study looked at the mass flux of EDCs in pilot-scale WWTPs (Esperanza et al., 2004). Here, mass flux was defined as the concentration of a certain EDC in the waste stream, multiplied by the flow rate of that waste stream. Two WWTPs were used; one with aerobic digestion of solids and one with anaerobic digestion of solids. Otherwise, both WWTPs had treatment trains consisting of primary and secondary sedimentation and a three-stage aeration tank. Supernatant effluent from the digester was mixed with dewatered filtrates from the primary clarifier and waste activated sludge, and metered into the primary clarifier as return flow (Esperanza et al., 2004). Dewatered primary and waste activated sludge was returned to the digester. Synthetic wastewater was used, with the concentrations of several estrogenic and androgenic hormones set at 100 ng/L. The hormones E1, E2, EE2, and E3 were the measured estrogenic hormones.

It was observed that for all EDCs tested, there was an increase in mass flux between the influent and primary clarifier effluent. For the aerobic digestion pilot plant, the E2 mass flux increased from 750 ng/h in the plant influent to 900 ng/h in the primary clarifier effluent (Esperanza et al., 2004). It was suggested by the authors that water entering the primary clarifier desorbed part of the target compounds from the solids (Esperanza et al., 2004). It is known that some amount of adsorption to solids was taking place due to the fact that theoretically, 2000 ng of estrogenic and androgenic hormones were entering the plant per hour (from the amount of hormone added to wastewater). Overall, anaerobic solids digestion proved to be marginally better at reducing mass flux. Influent concentrations were slightly higher for the aerobic digestion WWTP than for the anaerobic WWTP. Whether this difference is enough to make a definitive statement regarding the advantages of one over the other is uncertain.

Another group of researchers examined the levels of E1, E2, and EE2 at various points in a municipal wastewater treatment plant in Wiesbaden, Germany (Andersen et al., 2003). The Wiesbaden plant had a treatment train consisting mainly of primary sedimentation, two denitrification tanks in series, nitrification, secondary sedimentation and sludge digestion. Sludge was recycled from secondary sedimentation to denitrification and from nitrification to denitrification. Excess secondary sludge liquid was recycled to the start of primary sedimentation, as was pre-thickened primary sludge. Samples were taken prior to primary sedimentation, after primary sedimentation, after each denitrification tank and nitrification and prior to discharge. Results may be seen in Table 4.

Table 4. Results of Wiesbaden WWTP sampling program (from Andersen et al., 2003)

Sampling location	Hormone concentration (ng/L)		
	Estrone	17β-Estradiol	17α-Ethinylestradiol
Raw wastewater	54.9 - 76.6	12.2 - 19.5	6.2 - 10.1
Primary sedimentation effluent	66.2 - 83.6	9.2 - 12.6	3.5 - 7.0
Denitrification tank 1 effluent	29.7 - 44.9	9.2 - 11.4	0.9 - 2.1
Denitrification tank 2 effluent	2.2 - 3.5	<1	1.1 - 1.3
Nitrification tank effluent	1.8 - 1.9	<1	<1
Secondary sedimentation effluent	<1	<1	<1

As seen in Table 4, dissolved hormone concentrations ranged from < 1 to 76.6 ng/L for E1, < 1 to 19.5 ng/L for E2, and < 1 to 10.1 ng/L for EE2. This is consistent with the environmental concentrations discussed previously. Of particular interest are the decreases seen following denitrification tank 2, which can be attributed to biological degradation (Andersen et al., 2003). Dilution was held to be mainly responsible for initial decreases in concentration, as it was noted by the authors that conjugated forms of the hormones were likely cleaved in the initial treatment stages, thus causing an increase in hormone concentration (Andersen et al., 2003). As well, E1 has been noted as being a metabolite of E2 (RSC, 1999). Indeed, an increase in E1 between the raw WW influent and primary clarifier influent can likely be attributed to partial degradation of E2 into E1.

One group of authors attempted to predict EDC removal from hydraulic retention time (HRT) and sludge retention time (SRT), using data gathered from 17 WWTPs (Johnson et al., 2005). These WWTPs comprised a wide range of treatment practices such as activated sludge, oxidation ditches, primary and chemical treatment only, combined trickling filter with activated sludge and submerged aerated filters (Johnson et al., 2005). There seemed to be an association between higher HRTs and SRTs and extent of EDC removal. It was felt that this indicated the importance of biological activity to EDC removal (Johnson et al., 2005). The authors also felt that higher microbial activity in wastewater treatment plants led to lower EDC effluent concentrations. Similarly, another group felt that there was a strong correlation between SRT and effluent concentrations, with a critical SRT being 10 days (Clara et al., 2005).

Another group of researchers attempted to define the effect of conventional water treatment technologies on eEDC concentrations (Westerhoff et al., 2005). Natural waters were spiked with E1, E2, E3 or EE2 and exposed to bench-scale alum, powdered activated carbon (PAC), hypochlorite, and ozone treatment. Alum dosages of 6.3 mg/L

(as Al^{3+}) removed 5% of E1 and 2% of E2, of an initial contaminant concentration of 100 ng/L. PAC doses of 5 mg/L removed 76% of E1, 84% of E2, 60% of E3 and 77% of EE2. Hypochlorite treatments of 3.5 and 3.8 mg/L (pH 5.5, 24 hour contact time) removed approximately 97% of all four contaminants. Ozone doses of 3 to 4 mg/L and a contact time of 3 minutes were sufficient to cause 98% to 99% removal of all four contaminants. From this experiment, it can be seen that alum and PAC were of limited use, and that oxidative treatment was both more effective and more consistent, although hypochlorite required an extensive contact time. It should be noted that this study examined treatments individually, not as part of a treatment train as was done with the mass-balance studies mentioned above.

Water and wastewater treatment technologies for removing eEDCs

There are a number of treatment technologies that have been used to deal with EDCs. In this review, research of interest is that research which has focused on the reduction of EDC concentration by means of ozonation and/or ozone-based advanced oxidation processes (AOPs). Other tested treatment technologies include membranes and AOPs utilizing catalysts such as Fenton's reagent and titanium dioxide (TiO_2), which shall be discussed briefly later on. Research has also been done with regards to reducing the estrogenicity of eEDCs, which shall also be discussed later.

Generally, treatment processes that can remove or degrade contaminants and that require the least amount of time and money are preferred. Also, those treatment processes that can treat a number of contaminants at the same time are also preferred. This is particularly relevant for micropollutants, such as eEDCs, pesticides, industrial reagents, etc. It is very unusual to have only one or less than half a dozen micropollutants in wastewater or surface water. It would be more likely to find a dozen or more contaminants present at very low concentrations, usually microgram per litre (μg/L) or nanogram per litre (ng/L) (Kolpin et al., 2002).

By-product toxicity and residual estrogenicity are extremely important parameters in choosing treatment methods. It is possible that a particular treatment method may cause the formation of more toxic by-products or breakdown products. This has been noted in biological treatment, particularly with alkylphenols, and in chlorination microorganism reduction, resulting in trihalomethanes (THMs) (Metcalf and Eddy Inc., 2003). Thus, any treatment method's resulting by-products and daughter products should be carefully considered.

Ozonation

One important feature of ozonation, or any process involving ozone, is its two main acknowledged reaction pathways. The most intuitive reaction pathway is the direct ozone reaction, which is the reaction that occurs between the ozone molecule and any chemical species, such as molecular products, free radicals, etc. (Beltrán, 2004). The second reaction pathway, is the indirect pathway, whereby the hydroxyl radical (which may be formed from the decomposition of ozone, or other direct ozone reactions), reacts with other compounds present in solution (Beltrán, 2004). It is important to note that ozone is an unstable molecule and thus both direct and indirect reactions are quite likely occurring at the same time. Moreover, ozone decomposition may be extremely complex and can involve numerous intermediate radicals; there are several proposed decomposition mechanisms, which may include different radical species (Beltrán, 2004). Ozone reactions are also very dependent on pH, with increasing pH causing an increased ozonation rate (Beltrán, 2004).

With regards to ozonation studies, one group used competitive kinetics to determine the rate constants for the degradation of EE2 via both direct and indirect ozone reactions (Huber et al., 2003). To determine the direct ozone-EE2 reaction rate constant, phenol was used as a reference compound. Work was done in the μM concentration range. The direct ozone reaction rate constant was found to be approximately 7×10^9 $M^{-1}s^{-1}$ at 20°C, pH 6. For determination of the hydroxyl radical reaction with EE2 rate constant, hydroxyl radicals were generated using a UV/H_2O_2 system and *p*-chlorobenzoic acid (*p*CBA) as a reference compound. The rate constant for the reaction of hydroxyl radicals with EE2 was found to be 9.8×10^9 $M^{-1}s^{-1}$ at 25°C, pH 7. It was the authors' opinion that the high rate constant ($> 5 \times 10^4$ $M^{-1}s^{-1}$) for the reaction of ozone with EE2 indicated that EE2 was completely transformed during ozonation (Huber et al., 2003).

Similar to the previous study, another group investigated the ozonation of EE2, E2, E1 and E3 (Deborde et al., 2005). Competitive kinetics was also used in this study, with phenol serving as a reference compound. The investigators varied pH in order to determine the effect of pH on the rate constants for the direct reaction of ozone with the contaminants (k_{O3}). For E1, it was found that k_{O3} was relatively constant at approximately 2×10^5 $M^{-1}s^{-1}$ between pH 2 and approximately 4.5. Between pH 4.5

and pH 10.5, k_{O3} increased from 2.5×10^5 $M^{-1}s^{-1}$ to 5×10^9 $M^{-1}s^{-1}$. After pH 10.5, k_{O3} appeared to level off. As a hydroxyl radical scavenger was used to consume any hydroxyl radicals present, it may be inferred that the observed effects are due to pH alone, rather than higher numbers of hydroxyl radicals brought on by the pH-mediated decomposition of ozone.

One group compared chlorination and ozonation in the treatment of E2 and EE2 (Alum et al., 2004). It was found that a chlorine dose of 1.0 mg/L reduced E2 and EE2 concentrations to below the detection level, after 1 hour of contact time. An ozone dose of 1.5 mg/L coupled with 1 minute of contact time reduced concentrations to below the detection limit of ~1 nM. The initial contaminant concentrations were 100 nM for both E2 and EE2, and detection limits were 1.15 nM and 0.96 nM for E2 and EE2 respectively. Estrogenicity of treated samples was also determined using the E-screen MCF-7 breast cancer cell assay (Alum et al., 2004). Response was referred to as the proliferation effect, which was defined as the ratio of cells produced by samples to the cells produced by hormone-free controls. A summary of the estrogenicity results for chlorination and ozonation may be seen in Table 5.

As seen in Table 5, increased dose or contact time did not necessarily lead to lower values for proliferation effect. For chlorination of E2, it can be seen that a dip in estrogenicity for the second-lowest dose was followed by a corresponding rise in estrogenicity for larger doses, with the end result being that samples treated with the most chlorine showed estrogenicity comparable to those treated with the lowest level of chlorine. A similar effect was seen for the ozonation of EE2, with the difference being that the estrogenicity of samples with the most contact time was higher than samples that had had the least contact time. The authors suggested that the momentary decline in estrogenicity was the result of transitional by-products (Alum et al., 2004). Also, chlorination of EE2 showed increases in estrogenicity as the chlorine dose increased.

Table 5. Summary of estrogenicity tests for chlorination and ozonation (from Alum et al., 2004)

Sample exposure	Proliferation effect (sample:control)	
Chlorination[a]		
Chlorine dose (mg/L)	**17β-estradiol (E2)**	**17α-ethinylestradiol (EE2)**
0.05	3.5	3.4
0.10	2.2	3.5
0.25	3.3	4.2
0.50	3.3	5.5
Ozonation[b]		
Contact time (min.)	**17β-estradiol (E2)**	**17α-ethinylestradiol (EE2)**
1	2.1	3.0
5	3.1	2.2
10	1.4	2.6
30	1.7	3.8
120	1.7	3.6

Note: a: Contact time of four days b: Dose of 1.5 mg/L

The authors also prepared a standard curve of proliferation effect using E2, and found that contaminant concentrations could not entirely account for the increase in estrogenicity (Alum et al., 2004). The authors thought that by-products or transitional products were contributing to estrogenicity (Alum et al., 2004). In the case of the E2 samples, E1 could likely have been a by-product of natural oxidation, as E2's transformation to E1 has been noted before (Andersen et al., 2003). This study demonstrated that merely reducing contaminant concentrations may not be sufficient to eliminate the threat posed by eEDC contaminated waters.

One group of researchers investigated the use of ozone to degrade E2 (Irmak et al., 2005). Ozone was bubbled directly into the sample solution and E2 concentrations were monitored for 90 minutes. It was found that the ozone/E2 molar ratio for the complete conversion of E2 was 8.89. The initial E2 concentration was 0.4 mM. A summary of the ozone doses and required oxidation time may be seen in Table 6.

Table 6. Ozone doses and oxidation time required for various percent removal of E2 (from Irmak et al., 2005)

Ozone Flow Rate ($\times 10^{-3}$ mmol/min)	Ozone Dose (mmol)	Oxidation Time (min)	E2 Removal (%)
15.78	0.868	55	100
12.25	0.919	75	100
9.78	0.880	90	100
8.22	0.740	90	87
7.56	0.680	90	70

From Table 6, it may be seen that 100% removal was achieved for the three highest doses. The amount of time required for oxidation (up to 90 minutes) may be attributed to the low ozone/contaminant ratio and low ozone flow rate.

Another group investigated the use of ozone to degrade E2 (Kamiya et al., 2005). It was found that the E2 concentration decreased from 100 μg/L to 0.05 μg/L, consuming 0.15 mg/L of ozone. Ozone was bubbled directly into the reactor for about 15 minutes. Through the use of reaction models and curve-fitting, a value of 2.0×10^5 $M^{-1}s^{-1}$ was obtained for the reaction rate of E2 and ozone (Kamiya et al., 2005). Change in sample estrogenicity was also assessed using a two-hybrid recombinant yeast assay, and it was found that β-galactosidase activity declined from 1250 to below the detection limit with 0.1 mg ozone consumed (Kamiya et al., 2005). Change in β-galactosidase activity was most significant between 0.08 mg/L and 0.1 mg/L ozone consumed, with activity dropping from approximately 1000 units to nearly detection level between those values.

A more recent study looked at the use of O_3 and O_3/H_2O_2 to treat a number of contaminants (including E1, E2, E3 and EE2) in both bench and pilot scale experiments (Snyder et al., 2006). Experiments were conducted using spiked surface water and wastewater effluent, and estrogenicity was determined using a human breast carcinoma in vitro bioassay (likely a variation of the MCF-7 bioassay). The four steroid hormones were spiked at levels ranging from 347 to 361 ng/L.

In spiked surface water, percent removal was above 95% for an ozone dose of 1.25 mg/L (Snyder et al., 2006). Little difference was seen between reaction time (ranging from 2 to 24 minutes) or among the different steroid hormones. Adding 0.25 mg/L H_2O_2 made seemingly little difference to hormone percent removal. Percent removals reported differed by less than 5%,

which may not necessarily be practically significant. Similar behaviour was seen in experiments utilizing an ozone dose of 2.5 mg/L and an H_2O_2 dose of 0.5 mg/L. The minimum percent removal in this case was 98%.

Bench top experiments performed with treated wastewater yielded varying results. Estriol and estrone were detected in the wastewater, ranging in concentration from < 5 ng/L to 5.7 ng/L and 5.4 ng/L to 20 ng/L, respectively. Ozone doses of 2.1 and 3.6 mg/L were relatively ineffective for estriol; an ozone dose of 7.1 mg/L was able to remove >94%, however. For estrone, it was seen that the addition of H_2O_2 improved treatment. At an ozone dose of 2.1 mg/L, percent removal increased from <1% to 44% with the addition of 1.0 mg/L H_2O_2. At an ozone dose of 3.6 mg/L, percent removal went from >81% to >94% with the addition of 2.5 mg/L H_2O_2, and percent removal at an ozone dose of 7.6 mg/L went from >91% to >94% with the addition of 3.5 mg/L H_2O_2.

Favourable results were also obtained in the same study for the removal of estrogenicity by O_3 and O_3/H_2O_2. Greater than 90% removal (measured in estradiol equivalent units) was achieved for ozonated tertiary effluent, at ozone doses ranging from 4.9 mg/L to 8.7 mg/L (Snyder et al., 2006). Addition of H_2O_2 seemed to improve percent removal, bringing increases of 66%, 6% and 3% at ozone doses of 2.1 mg/L, 3.6 mg/L and 7.1 mg/L, respectively.

Overall, the authors felt that the addition of H_2O_2 may increase the rate of contaminant decomposition, but not necessarily overall removal (Snyder et al., 2006). The authors also noted that the apparent gains in estrogenicity removal as a result of H_2O_2 addition may be due to varying initial estrogenicity between the O_3 and O_3/H_2O_2 experiments.

Emerging EDC treatment methods – AOPs with O_3, H_2O_2 and UV

While other treatment, particularly membranes, have been the focus of numerous work regarding EDCs, the use of AOPs involving ozone, hydrogen peroxide and ultraviolet radiation has gained attention in recent years. AOPs are known to be particularly applicable to the treatment of micropollutants, which EDCs could be considered to be. As well, the combination of O_3 with H_2O_2 and UV could potentially prove to be very powerful for oxidizing due to the enhanced production of $^{\cdot}OH$ radicals. Advanced oxidation processes with O_3, H_2O_2 and UV (non-

catalytic AOPs) have been investigated for use in treating textile wastewaters, particularly wastewaters resulting from dyeing and rinsing processes (Georgiu et al., 2002; Sevimli and Sarikaya, 2002; Hsu et al., 2003). As municipal water and wastewater treatment applications are the focus of this review, such applications shall not be discussed. Treatment combinations that have been the subject of published work shall be addressed.

2.6.1 AOPs with UV and H_2O_2

One group investigated the use of UV/H_2O_2 treatment to degrade EE2, and E2 (Rosenfeldt and Linden, 2004). It was found that a H_2O_2 dose of 15 mg/L and a UV fluence of 1000 mJ/cm^2 degraded greater than 95% of EE2, and E2, for both low and medium pressure lamps. Low-pressure UV lamps alone degraded 2% and 5% of EE2, and E2, respectively. Medium pressure lamps alone degraded 21% and 18% of EE2, and E2, respectively. Hydroxyl radical rate constants for EE2 and E2 were found to be 1.08×10^{10} and 1.41×10^{10} $M^{-1}s^{-1}$, respectively. Quantum yields for the aforementioned compounds were 0.026 and 0.043 mol/Es, respectively with low pressure lamps, and 0.061 and 0.10 mol/Es, respectively with medium pressure lamps.

2.6.2 AOPs with UV and O_3

Another group of researchers investigated the use of ozone (described previously) and ozone/UV processes to treat E2 (Irmak et al., 2005). Analytes were quantified using high-performance liquid chromatography (HPLC). Ozone was bubbled directly into the sample solution and a 15 W low pressure mercury lamp was immersed in the reactor. E2 concentrations were monitored for 90 minutes, and were initially 0.4 mM. It was found that with the addition of photolysis, the ozone/E2 molar ratio for the destruction of E2 was reduced to 6.64 and that the required time for E2 destruction had decreased (Irmak et al., 2005). A summary of the ozone doses and required oxidation time may be seen in Table 7.

Table 7. Required ozone doses for destruction of E2 in Ozone/UV treatment system (from Irmak et al., 2005)

Ozone Flow Rate (x 10^{-3} mmol/min)	Ozone Dose (mmol)	Oxidation Time (min)	E2 Removal (%)
15.89	0.715	45	100
12.21	0.672	55	100
9.78	0.655	67	100
8.22	0.616	75	100
7.56	0.680	90	92

From Table 7, it can be seen that the addition of photolysis increased the rate of E2 degradation as compared to the data shown in Table 6, enabling complete removal to be achieved in shorter time frames. That being said, the sensitivity of the analytical method used is unknown – it is possible that the resulting effluent had E2 concentrations close to or greater than environmental levels, but were below the analytical method's limit of detection. Nevertheless, it is apparent that adding combining UV irradiation and ozonation reduced both required contact time and required ozone dose.

2.7 UV

UV alone cannot be considered an AOP, as it does not generate hydroxyl radicals. That being said, it is a fairly well-established treatment method, and is worth discussing.

A group of researchers looked at the use of UV to degrade pharmaceuticals and estrogens in both purified water and river water (Lin and Reinhard, 2005). A photosimulater with a 1.1 kW xenon arc lamp was used to irradiate E2, E3, E1, and EE2 in concentrations between 1 and 2 μg/L. Irradiation intensity was set at a maximum of 765 W/m^2. The purified water used was Milli-Q water and the river water came from the Santa Ana River and had dissolved organic carbon concentration of 4.6 mg/L, pH of 7.5 and a nitrate concentration of 22.3 mg/L.

It was seen that for all estrogens, higher photolysis rate constants were seen in river water than in Milli-Q water. E2, E3 and EE2 all had a photolysis rate constant of 0.02 h^{-1} in Milli-Q water. E2 had a photolysis rate constant of 0.35 h^{-1} in river water and E3 had a photolysis rate constant of 0.24 h^{-1} in river water. E1 had a photolysis rate constant in Milli-Q of 0.15 h^{-1} and 0.31 h^{-1} in river water. EE2 had a photolysis rate constant in river water of 0.30 h^{-1}. It is interesting that higher rate

constants were obtained in river water, as natural water matrix constituents are usually viewed as being detrimental to treatment. The authors attributed the increased degradation to photosensitization by dissolved organic matter (DOM) in the river water (Lin and Reinhard, 2005). The authors noted that DOM has been known to act as a precursor for photoreactive species which would then increase the overall rate of photolysis (Lin and Reinhard, 2005).

Another group of researchers compared the use of a UV disinfection lamp (presumably a low pressure lamp) and a high pressure mercury lamp to photolyze E1 and E2 (Liu and Liu, 2004). The disinfection lamp was 30 W, produced a maximum wavelength of 253.7 nm and an intensity of 1500 $\mu W/cm^2$. The HP mercury lamp was 125 W, produced wavelength greater than or equal to 365 nm and a light intensity of 14,000 Lux. It was found that the HP lamp reduced E1 concentrations to 5% of the original value within 60 minutes of irradiation, and reduced E2 concentrations to 45% of the original value within 60 minutes of irradiation. The disinfection lamp achieved only a nominal reduction in E2 concentration over 60 minutes of irradiation, but reduced the E1 concentration to half of its original concentration over 60 minutes. The authors theorized that the primary degradation mechanism was destruction and breakage of the substituted benzene ring found in both compounds, with the end result being the production of compounds containing carbonyl groups (Liu and Liu, 2004). Pseudo-first order rate constants were also determined, and it was found that initial concentrations of 3.0 to 20.0 mg/L yielded rate constants in the range of -0.03019 to -0.01395 for E2 and -0.01489 to -0.00762 for E1 (units presumed to be min^{-1}).

The same group of authors also investigated the effect of pH on contaminant degradation rate products (Liu and Liu, 2004). Plots of *k* versus pH showed a slightly sinusoidal relationship, with each contaminant exhibiting a minimum *k* at pH 5, and a maximum *k* at pH 8. For E1, the minimum *k* was 0.0085 min^{-1} and the maximum 0.0125 min^{-1}. For E2, the minimum *k* was 0.0135 min^{-1} and the maximum was 0.016 min^{-1}.

2.8 Catalytic AOPs

Although they are not the focus of the review, or of the overall experiment, it is worth mentioning catalytic AOPs. Catalytic AOPs are so named because they often utilize solid phase reagents or catalysts, such as Fenton's reagent, or TiO_2. Catalytic AOPs may also be heterogeneous, (such as TiO_2) meaning they occur in more than one phase.

Catalytic AOPs may often include UV in treatment. One example is a photo-Fenton study performed by Feng et al. (2005), in which a 250 W metal halide lamp was used to irradiate an E1 Fenton treatment system. Various combinations of UV, Fenton's reagent (Fe(III) as $FeCl_3 \cdot 6H_2O$ and H_2O_2) were used. It was found that a combination of all three was the most effective, degrading 98.4% of E1 in 160 minutes. Degradation increased as concentrations of Fe(III) and H_2O_2 increased, and as pH decreased (Feng et al., 2005).

TiO_2 treatments require the use of UV. One study by Ohko et al. (2002) looked at the use of TiO_2 photocatalysis to degrade E2 and reduce estrogenicity. TiO_2 powder was dissolved in E2 solution, and the reaction vessel was instantly irradiated by 365 nm band pass filtered light from a 200 W mercury xenon lamp (Ohko et al., 2002). Irradiation intensity was found to be 6 $mW \cdot cm^{-2}$ by using a radiometer. It was found that over 99% of the E2 was degraded after 30 minutes of UV irradiation, and that treated samples displayed negligible intermediate estrogenicity, as determined by a yeast assay (Ohko et al., 2002).

3. Materials and methods

3.1. Materials

Reagents used were E1, phenol, *t*-butanol (also referred to as *tert*-butyl alcohol, TBA), acetophenone and methanol. E1 and phenol were 99% and 99.5% purity respectively, both purchased from Sigma-Aldrich (St. Louis, MO). Acetophenone was purchased from Fisher Scientific (Fair Lawn, NJ). TBA was purchased from Aldrich Chemicals (Milwaukee, WI). The methanol used was HPLC grade, purchased from Fisher Chemicals, Canada.

Ozone was generated using a Wedeco ozone generator, model GSO 30 supplied with compressed oxygen (Wedeco, Herford, Germany). Ozone concentrations were determined using an Ultrospec 2100 *pro* spectrophotometer, manufactured by Biochrom Ltd (Cambridge, England). Ultrapure water used in the experiment was obtained from a Millipore system (Molsheim, France), and an Elga system (High Wycombe, UK).

The gas-tight syringes used to deliver oxidant dose were 2.5 mL, manufactured by Hamilton (Reno, NV). The stir bars used were Nalgene 10 mm star head stir bars, manufactured by Nalge Nunc International (Rochester, NY), purchased from Fisher Scientific. E1 stock was filtered using Osmonics AcetatePlus supported 50 mm filters, with a pore size of

0.45 μm (Minnetonka, MN). Experimental reactors used were 20 mL glass scintillation vials.

3.2. Preparation of ozone demand free materials

In order to eliminate instantaneous ozone demand, materials were made ozone demand free (ODF). ODF water was used for stock preparation and material rinsing, and was produced by bubbling ozone gas through demineralised water for at least 20 minutes (demineralised water obtained from Elga and Millipore systems). The resulting solution was set aside and agitated periodically until the smell of ozone had dissipated (around 1 to 2 days).

Pipet tips were made ODF by rinsing with ozone stock a minimum of three times, then were left to dry wrapped in aluminium foil. The gas tight syringes used for oxidant addition were initially made ODF by soaking the disassembled syringes overnight in ozone stock. After a number of runs had been performed, a practice was adopted whereby the syringes were rinsed with ozone stock a minimum of three times after experimental work had been completed for the day.

As the same stir bars were used from run to run, it was necessary to clean the stir bars in order to prevent cross-contamination from run to run. After a run had ended, and the sample vials were no longer needed, the stir bars were removed from the sample vials. Each stir bar was rinsed with methanol, then ODF water, so as to remove any traces of E1 or other experimental reagents. The resulting rinsate was discarded to E1 waste. The rinsed stir bars were then immersed in ozone stock and left overnight. Likewise, reactor vials and caps were also immersed in ozone stock and left overnight prior to use, although they were not reused as the stir bars were.

3.3. Preparation of E1 stock solution

E1 is known to have low solubility in water. Other researchers have found a range of values in the literature, and obtained solubility limits in the range of 1.24 mg/L to 2.27 mg/L over various pH levels (Shareef et al., 2006). Thus, due to the limited solubility of E1, and the need to have concentrations high enough to read with the HPLC apparatus, it was decided to prepare E1 stock to excess.

E1 stock solution was prepared by dissolving excess E1 in a 1 L, ODF amber glass bottle. The amount dissolved was equivalent to 10 μM concentration in 900 mL of ODF water. A stir bar was placed in the

bottle. The bottle was suspended by clamps in a larger glass beaker partially filled with water. The beaker with the bottle suspended in it was placed on a combination stirring/heating plate. The beaker was heated until the temperature reached a minimum of 60°C (maximum 80°C), and this temperature was sustained for a minimum of half an hour. The heat was then turned off, and the beaker/bottle apparatus was allowed to cool to room temperature. Stirring was continuous.

When the solution was needed, the E1 solution was filtered via an ODF vacuum filter apparatus with filter paper, to remove un-dissolved E1. The glass portions of the apparatus (filter flasks, filter cup, filter stone) were made ODF by either submerging in ozone stock or filling with ozone stock. The vacuum tubing did not contact the stock solution and thus was not made ODF. The filter paper was 0.45 μm.

Although the stock had been prepared to 10 μM concentration, the low solubility of E1 in water made it unlikely that the resulting stock would have a concentration of 10 μM. Thus, it was decided to filter the stock solution so as to remove any undissolved E1, and then use the filtered stock's concentration. The filtered stock concentration was determined using HPLC analysis; the stock sample was analyzed in triplicate. Over time, E1 concentrations declined in the stock, likely due to sorption on the glass bottle containing the stock. Stock solutions prepared for the experiment ranged in concentration from 2.54 μM to 6.62 μM (raw data in Appendix A).

3.4. HPLC analysis

All samples and stock concentrations were determined via high-performance liquid chromatography (HPLC) analysis, performed on a LC 10AT VP Shimadzu system. The HPLC system consists of a LC-10AT VP pump, a SCL-10A VP controller, a DGU-14A degasser unit, and a Shimadzu 10AV VP UV-vis detector. The HPLC column used was a Phenomenex Gemini 5 μm C18 110A column, with a size of 250 × 4.6 mm (manufactured by Phenomenex, Torrance, CA). All gradients were filtered using 0.2 μm or 0.45 μm filter paper.

The analytical method used was developed from one presented by Peñalver et al (2002). Due to the concerns regarding E1 solubility, methanol was added to the HPLC sample vials to act as a co-solvent, so that 50% (by volume) of the sample vials' contents were methanol. E1 and acetophenone standards were prepared entirely in methanol, and thus did not require any co-solvent. Phenol standards were prepared entirely in Millipore water, and did not have any co-solvent. HPLC analysis was manual injection for all experiments, and the method was

altered several times. The final method used for the direct ozone-E1 rate reaction experiments (Part I) was a gradient elution scheme, consisting of 35% acetonitrile, 65% water for zero to five minutes and increasing to 65% acetonitrile by six minutes. 65% acetonitrile was maintained until 12 minutes, at which time the gradient was decreased, returning to 35% acetonitrile by 16 minutes. Runs were ended at 17.5 minutes. HPLC results for Part I standards and the resulting standard curves may be seen in Appendix A. Corresponding information for Part II may be found in Appendix D. HPLC results for E1 stock analysis may also be found in Appendix A. Sample chromatograms for selected standards may be seen in the following figures.

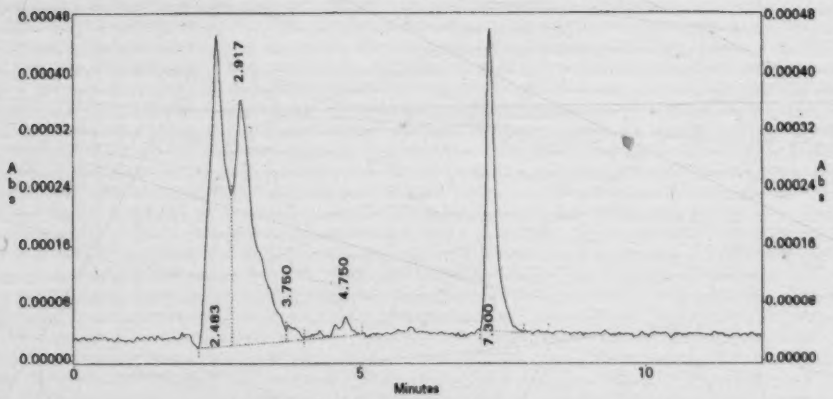


Figure 2. HPLC chromatogram for 2 μM E1 standard (O_3 experiments).

As seen in Figure 2, the absolute absorbance in the HPLC chromatograms is rather low (less than 0.00048 AU). The E1 peak can be seen at a retention time of 7.300 minutes; the large peak area prior to that likely represents methanol, as the E1 standards were prepared in methanol. It should be noted that these standards were analyzed using the initial method, and therefore E1 had a different (later) retention time during the experiments.

An example of the phenol standards may be seen in Figure 3. As seen in Figure 3, the absolute absorbance in this HPLC chromatogram is also quite low (slightly larger than 0.0006 AU). The phenol peak can be seen at a retention time of 4.283 minutes, although, as with E1 above, this was to change during the subsequent experiments. The peak and valley area prior to phenol is considered an artefact.

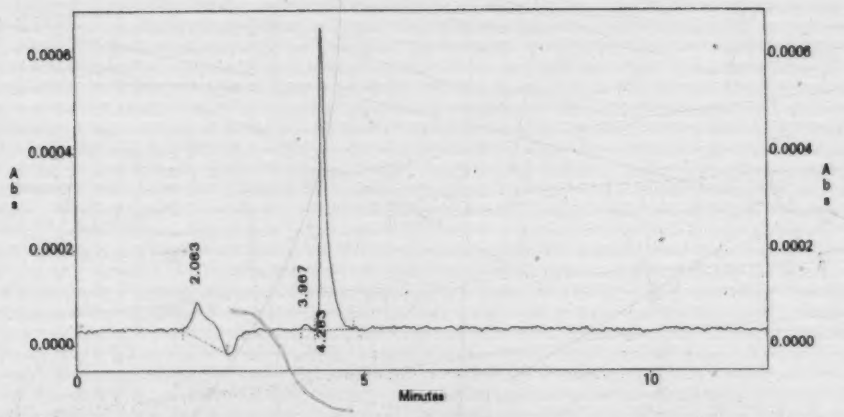


Figure 3. HPLC chromatogram for 2.5 μM phenol standard, Part I (O_3 experiments).

Analysis for each individual sample was repeated three to four times. If the first three analyses yielded a standard deviation that was more than 5% of the average, a fourth analysis was performed. The results were averaged, and the average value used for rate constant calculations. The Q-test (Shoemaker et al., 1974) was used (at the 90% level) to exclude outliers from the HPLC analyses. The run was discarded and analysis performed again if a HPLC run showed a quantifiable peak for one compound of interest, but not the other. HPLC analysis was generally completed within 48 hours of sample preparation; it was felt that this time frame afforded the least amount of run-to-run variability.

The HPLC method was altered for the hydroxyl radical – E1 reaction experiments (Part II). As a different reference compound was adopted (acetophenone rather than phenol), it was beneficial to alter the method to suit the new reference compound. The elution scheme and run time were altered; acetonitrile content was increased to 50%, and the elution was made isocratic. The run was initially terminated at 15 minutes; later it became apparent that it could be terminated at 14 minutes. Even later in the experiments, the runs were terminated at 13 minutes; however, a shift in E1 retention time following HPLC service required the run length to be moved back to 14 minutes. Sample chromatograms for selected standards may be seen in the following figures.

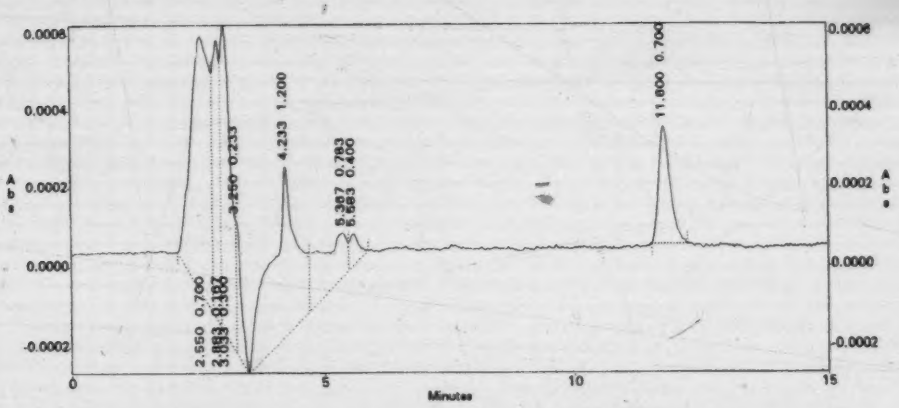


Figure 4. HPLC chromatogram for 2 μM E1 standard (·OH experiments).

As seen in Figure 4, the E1 peak appears at 11.8 minutes. Again, the large peak/valley complex beginning around 2.5 minutes is believed to be methanol, and possibly some residual artefacts. The E1 standard curve was developed anew for Part II, as it was felt that the change in analytical method could possibly have an effect on peak area.

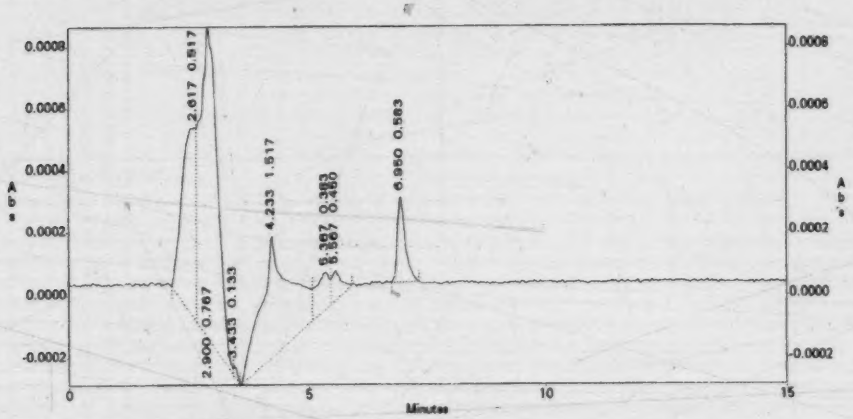


Figure 5. HPLC chromatogram for 2.5 μM acetophenone standard (·OH experiments).

As seen in Figure 5, the acetophenone peak appears at 6.950 minutes. Since the acetophenone standards were prepared in methanol, the methanol complex also appears in the acetophenone standards.

3.5. Experimental apparatus

For Part I, contaminant (E1), reference compound (phenol), scavenger (TBA) and buffer were placed in 20 mL glass scintillation vials. Phenol, scavenger and buffer were added first to the vials. A 10 mm star head stir bar was added to each vial, and the vials were then put on a magnetic stir plate to stir. After the vial contents were stirring, E1 was added. Due to concerns regarding E1 solubility, it was deemed necessary to have the vial contents stirring continuously from the addition of E1 to the sample vials, until the experiment was over and the vial contents had been sampled for HPLC analysis.

Each sample vial contained 15 mL of E1 and 1 mL each of phenol, TBA and phosphate buffer (buffer stock either 100 mM or 250 mM). The experimental protocol called for 1 mL of ozone stock and 1 mL of hydrogen peroxide stock (both of varying concentrations) to be added to the sample vials via 2.5 mL gas tight syringes. For the control vial, 2 mL of ODF water was added during experimental preparation, in lieu of the oxidant solutions. Each experimental run had five sample vials: one control, and four oxidated samples. The oxidated samples received varying oxidant doses. For the direct ozone-E1 rate reaction experiments, H_2O_2 doses ranged from 200 μM to 10 μM and ozone doses ranged from 240 μM to 25 μM. For Part II, H_2O_2 doses ranged from 100 μM to 5 μM and ozone doses ranged from 120 μM to 12.5 μM. A summary of the oxidant concentrations used may be seen in Appendix A.

Hydrogen peroxide stock of the desired concentrations had been prepared prior to the runs. Knowing the O_3/H_2O_2 ratio for each experimental run, one could then determine the required ozone concentration for each dose. The H_2O_2 concentrations were chosen so that the combined O_3/H_2O_2 concentration would not exceed 300 μM for the highest dose in Part I, or 150 μM for the highest dose in Part II.

Required ozone concentrations were obtained by diluting ozone stock with ODF water. Ozone concentrations were determined using a spectrophotometer set at 260 nm. After addition of ozone and hydrogen peroxide, vials were kept stirring for a minimum of 15 minutes (30 preferred) to ensure that all oxidants were completely consumed before sampling for HPLC.

The hydroxyl radical rate reaction experiments were conducted in a very similar manner, with the main exception being the absence of any scavenger. In the place of TBA, 1 mL of ODF water was added to the sample vials.

3.6 Competitive kinetics

The experimental method of competitive kinetics, as described by Beltrán (2004) and used by Huber et al. (2003), was used here to determine rate constants between contaminants and oxidants. Competitive kinetics is usually used when the expected rate of reaction between a contaminant and an oxidant is too fast to be measured by conventional means such as direct rate measurement. In direct rate measurement, a contaminant is exposed to oxidant(s) and samples are withdrawn at various time intervals and analyzed for contaminant concentration, enabling the determination of the rate of reaction between contaminant and oxidant(s). In competitive kinetics, however, a contaminant is placed in a reactor with a known quantity of a reference compound, which has a known rate of reaction with the oxidant of interest. Varying doses of oxidant are introduced into a series of such reactors, and the reactor contents are sampled after a certain amount of time. The contaminant and reference compound concentrations are in excess of the stoichiometric oxidant/contaminant ratio, and the oxidant is thus assumed to be completely consumed in the reaction, which means that the experiment only continues until all oxidant has been consumed. At the end of the test, samples are analyzed to determine the remaining concentrations of contaminant and reference compound. Data are evaluated by the following equation, where $k_{oxidant}(R)$ and $k_{oxidant}(M)$ are the rate constants for the reaction of oxidant with the reference compound (R) and the contaminant (M), respectively (Huber et al., 2003). The various oxidant doses are represented by n, with 0 representing zero oxidant dose (control) (Huber et al., 2003). Thus, the contaminant concentration at a particular oxidant dose is represented $M(n)$, and the reference compound as $R(n)$.

$$\ln\left(\frac{[M(n)]}{[M(0)]}\right) = \ln\left(\frac{[R(n)]}{[R(0)]}\right)\frac{k_{oxidant}(M)}{k_{oxidant}(R)}$$

It can be seen that the form of this equation is similar to the equation $y = mx$, which is commonly used to represent linear equations. By graphing $\ln(M(n)/M(0))$ as y and $\ln(R(n)/R(0))$ as x, the slope of the resulting straight line can be taken to equal $k_{oxidant}(M)/k_{oxidant}(R)$. Knowing $k_{oxidant}(R)$, one can then determine $k_{O3}(M)$. For experiments investigating direct ozone oxidation, a parameter called z_{rel} is added to the right side of the equation above. The parameter z_{rel} is the ratio of stoichiometric coefficients of the ozone-E1 and ozone-phenol reactions (Beltrán, 2004).

In these experiments, $k_{oxidant}(M)/k_{oxidant}(R)$ was taken as equal to the slope of the best fit line drawn in Excel. The axis intercept (b) was set to zero, so that the resulting best fit line equation would be of the same

form as the competitive kinetics equation shown above. Sample calculations may be found in Appendices C and F.

While competitive kinetics is often used without any stated assumption of the reaction order, the resulting rate constant is held to be second order. Previous research regarding ozone-solutes reaction have found the reaction to be first order with respect to ozone and first order with respect to the solute in question, thus yielding an overall second order reaction (Hoigné and Bader, 1983a). This enables the absence of run time as an experimental factor.

When ozone is used as the oxidant, however, rate constants are determined for only one of the two reaction pathways at a time: the direct ozone reaction or the hydroxyl radical reaction (hydroxyl radicals resulting from the decomposition of ozone). Numerous reference compounds, such as *p*CBA, acetophenone, and atrazine, react strongly with ozone via one pathway, and almost negligibly via the other pathway (Beltrán, 2004). Thus, competitive kinetics experiments involving ozone often give the rate of reaction for one pathway.

Some oxidation would still take place via the secondary pathway, and would give false reaction constants. In order to eliminate this possibility, scavengers (usually one per experiment) are often included in ozone competitive kinetics experiments. The scavengers have a very high rate of reaction with the secondary mechanism, thus ensuring that observed contaminant destruction is due only to the mechanism of interest. For example, if one were studying the rate of reaction between a contaminant and the direct ozone mechanism, the hydroxyl radicals resulting from ozone auto-decomposition would be the secondary, interfering pathway. A scavenger that reacts strongly with hydroxyl radicals but not with ozone or to a negligible amount (such as TBA) would be added to consume any hydroxyl radicals generated, leaving the direct ozone- contaminant reaction to proceed without any interference or outside influence.

For Part I, phenol was used as the reference compound, and TBA was used as the hydroxyl radical scavenger. This is the same approach taken by Huber et al. (2003). For Part II, acetophenone was used as the reference compound. No scavenger was used, as acetophenone reacts very slowly with ozone (3.5 $M^{-1}s^{-1}$) (Acero et al., 2000). This means that Part II is not an orthodox competitive kinetics experiment, as both direct ozone and hydroxyl radical oxidation of E1 would occur during the experiments. Issues arising from this approach will be discussed later on.

4. Results and discussion

4.1. Analytical method development

Initially, isocratic elution was used, 60% acetonitrile and 40% deionized water with a 15 min. run time for E1 and phenol analysis. While this proved effective for the phenol and E1 standards, it was not sufficient for the experimental samples. The methanol included in the samples to preserve solubility produced a group of peaks early in the elution and acted to present a shoulder effect that overlapped with the elution of phenol. An example of this shoulder effect may be seen in the following figure.

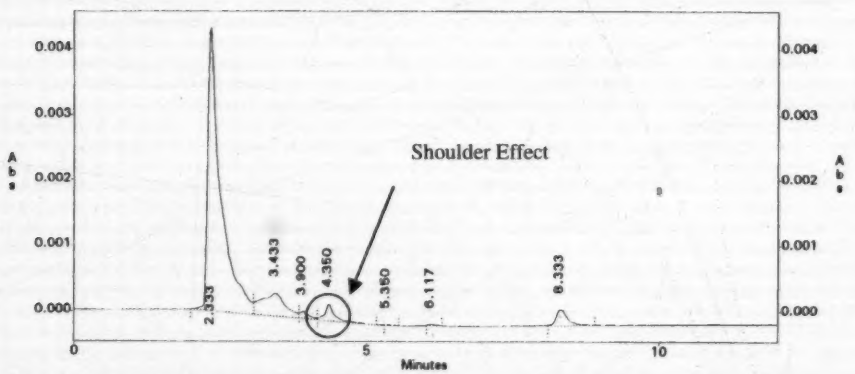


Figure 6. HPLC run chromatogram, showing shoulder effect (O_3 experiments).

As seen in Figure 6, a shoulder effect can be seen on the phenol peak, at 4.350 minutes. As this complicated peak quantification, the analytical method was changed. Thus, acetonitrile volume was reduced to 55%, then 50% so as to resolve overlapped peaks.

Further on during the direct ozone experiment, a "double peak" phenomenon emerged, which saw the phenol peak overlap with an unidentified peak. This unidentified peak was thought to be an oxidation by-product, most likely an oxidation by-product of phenol eluted at the same time as phenol, making the quantification of phenol difficult and error-prone. The HPLC method was altered yet again so as to definitively separate these two peaks; a gradient elution was used, as described previously in section 3.4. The elution described in section 3.4 was used for the remainder of the Part I experiments.

4.2. Experimental results (parts I and II)

4.2.1 Results, Part I (O_3 experiments)

A sample output from Part I can be seen in the following figure. HPLC run results for Part I may be found in Appendix B.

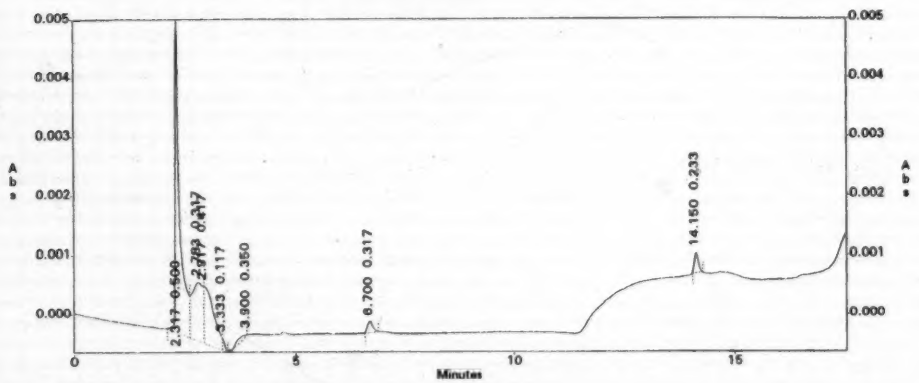


Figure 7. Sample chromatogram for Part I: replicate 1, run 6, pH 8.5, O_3/H_2O_2 = 4:1.

As seen in Figure 7, the absolute values of the analytes' absorbance (phenol at 6.700 minutes, E1 at 14.150 minutes), is small, particularly when compared to the methanol peak. The increasing slope starting about 11.5 minutes is thought to be the increased acetonitrile content (from the gradient elution scheme) reaching the detector.

Examples of the results of the competitive kinetics tests can be seen in the following figures. By using the slope of the best fit line, one can obtain the rate constants for the reaction of the contaminant with the oxidant. As seen in Figure 8, results obtained from competitive kinetics tests are not always of the greatest quality.

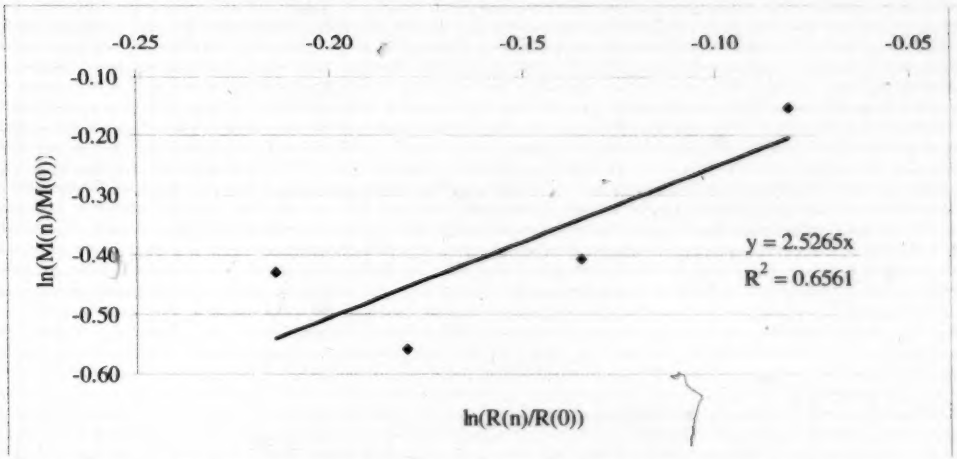


Figure 8. Replicate 1, run 1: pH 7, O_3/H_2O_2 = 2:1 (O_3 experiments).

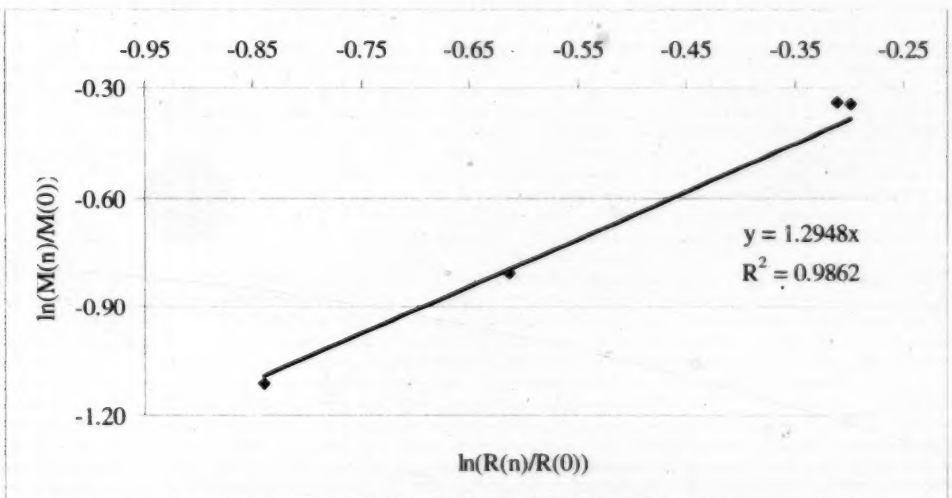


Figure 9. Replicate 1, run 6: pH 8.5, O_3/H_2O_2 = 4:1 (O_3 experiments).

Figure 9 shows an example of a run with better overall results. For the experiments described in this thesis, higher r^2 values were held to indicate better linearity. Run results were originally analyzed with an intercept in the best-fit line equation, and were included if the r^2 value for the graph was greater than 0.75, or if it was the closest to 0.75 of all the runs for those particular conditions. The results were subsequently re-analyzed with an intercept set to zero; the runs that had been previously deemed acceptable were included regardless of the value of the "new" r^2.

It should be noted that setting the intercept to zero reduced the r^2 value in all cases.

A summary of the obtained rate constants for the direct ozone experiments may be seen in the following tables. Obtained rate constants for Part I may be seen in Appendix C.

Table 8. Summary of rate reactions for Part I, pH 4

pH 4				
O_3/H_2O_2	$k_{O3\text{-}E1}$ ($M^{-1}s^{-1}$)			
	Replicate 1	**Replicate 2**	**Average**	**Standard deviation**
1:2	4.48×10^3	2.82×10^3	3.65×10^3	1.18×10^3
2:1	3.68×10^3	8.46×10^3	6.07×10^3	3.37×10^3
4:1	4.47×10^3 1.15×10^4	7.84×10^3 -	7.93×10^3	3.50×10^3

As seen in Table 8, average rate constants for pH 4 range from 3.65×10^3 $M^{-1}s^{-1}$ at an O_3/H_2O_2 ratio of 1:2, to 7.93×10^3 $M^{-1}s^{-1}$ at an O_3/H_2O_2 ratio of 4:1. Standard deviation ranges from 1.18×10^3 $M^{-1}s^{-1}$ to 3.50×10^3 $M^{-1}s^{-1}$.

Table 9. Summary of rate reactions for Part I, pH 7

pH 7				
O_3/H_2O_2	$k_{O3\text{-}E1}$ ($M^{-1}s^{-1}$)			
	Replicate 1	**Replicate 2**	**Average**	**Standard deviation**
1:2	7.73×10^5	6.64×10^5	7.19×10^5	7.71×10^4
2:1	1.13×10^6	8.73×10^5	1.00×10^6	1.81×10^5
4:1	1.39×10^6	7.86×10^5	1.09×10^6	4.26×10^5

As seen in Table 9, average rate constants for pH 7 range from 7.19×10^5 $M^{-1}s^{-1}$ at an O_3/H_2O_2 ratio of 1:2, to 1.09×10^6 $M^{-1}s^{-1}$ at an O_3/H_2O_2 ratio of 4:1. Standard deviation ranges from 7.71×10^4 $M^{-1}s^{-1}$ to 4.26×10^5 $M^{-1}s^{-1}$.

Table 10. Summary of rate reactions for Part I, pH 8.5

pH 8.5				
O_3/H_2O_2	$k_{O3\text{-}E1}$ ($M^{-1}s^{-1}$)			
	Replicate 1	**Replicate 2**	**Average**	**Standard deviation**
1:2	1.68×10^7	1.80×10^7	1.74×10^7	8.99×10^5
2:1	2.57×10^7	2.08×10^7	2.32×10^7	3.42×10^6
4:1	2.16×10^7	2.03×10^7	2.10×10^7	9.22×10^5

As seen in Table 10, average rate constants for pH 8.5 range from 1.74×10^7 $M^{-1}s^{-1}$ at an O_3/H_2O_2 ratio of 1:2, to 2.32×10^7 $M^{-1}s^{-1}$ at an O_3/H_2O_2 ratio of 2:1. Standard deviations range from 8.99×10^5 $M^{-1}s^{-1}$ to 3.42×10^6 $M^{-1}s^{-1}$.

From the tables above, it is apparent that a definitive O_3/H_2O_2 ratio effect is lacking. It can also be seen that there is a very definite pH effect seen, as rate constants vary by several orders of magnitude between pH levels. Two different sources of this effect may be considered: the pH effect on ozonation and the pH effect on E1 itself. It has been noted that both direct and indirect ozone reactions are dependent on pH, and that an increase in ozonation rate is often seen with an increase in pH (Beltrán, 2004). Thus, an increase in rates of reaction as pH increases would be expected in any case, regardless of the contaminant in question.

The second possible source of the pH effect, that of pH's effect on E1, is also potentially substantial. Dissociating compounds are generally expected to behave differently at different pHs; a dissociated form of a compound often displays differing reactivity than the parent compound. E1 is indeed a dissociating compound, with a pK_a value similar to that of EE2, which has a pK_a 10.4 (Huber et al., 2003). Thus, one would expect E1's reactivity to increase as the solution pH neared E1's pK_a value, and certainly, the increasing rate constants at higher pH seem to bear this out.

Further explanation for the pH effect can be found in the behaviour of phenol. Phenol has a pK_a value of approximately 9.9 (Weber et al., 2004). Phenol is also a dissociating compound, and it has been noted that the reactivity of phenol increases as pH increases (Beltrán, 2004). This is useful information because E1 and the other estrogenic steroid hormones (E2, E3 and EE2) have a phenolic structure; they have sometimes been referred to as phenolic hormones (Huber et al., 2003). With similar structures,

one could reasonably expect to that E1 and phenol would behave in a similar manner, particularly with respect to pH.

That being said, it is worth considering whether the pH seen in the experiments is sufficiently high so as to cause notable dissociation. One can approximate the degree of dissociation using an equation given for phenol:

$$\alpha = \frac{1}{1+10^{pK-pH}} \qquad \text{(Beltrán, 2004)}$$

where α represents the degree of dissociation. Using a pK_a of 10.4 for E1, and the highest experimental pH value of 8.5, one obtains a degree of dissociation of approximately 1.24%. Whether this is sufficiently large so as to cause a practical difference, is unknown. It cannot be said, therefore, that E1 dissociation is the main cause of rate constants increasing as pH increases. It should be noted, however, that since phenol has a lower pK_a value, it would dissociate more than E1 at the same pH.

It may be seen from the previous tables of rate constants that the standard deviations of the rate constants are also large, often only one order of magnitude less than the rate constants themselves, or of the same order of magnitude. This is no doubt due to the fact that the average rate constants consist of two replicates only; the standard deviation is therefore only the difference between the two replicates. Also, the variability of the rate constants is no doubt contingent on the inherent variability of the competitive kinetics method itself.

4.2.2. Results, Part II (·OH experiments)

A sample output from Part II may be seen in the following figure. HPLC run results for Part II may be seen in Appendix E.

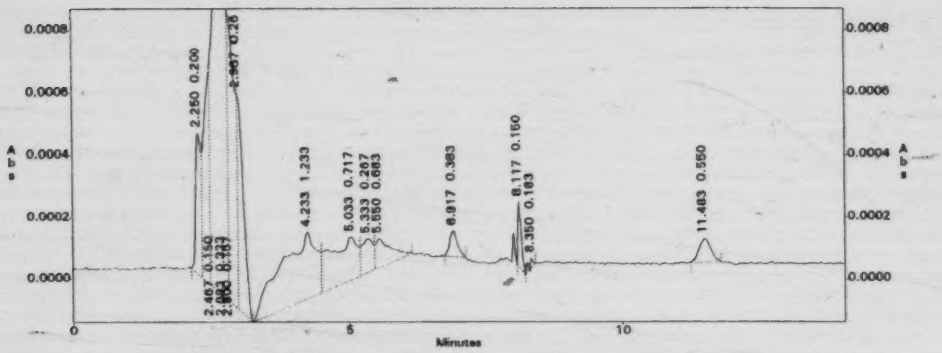


Figure 10. Sample chromatogram for Part II: replicate 1, run 7: pH 8.5, $O_3/H_2O_2 = 2:1$.

A summary of the obtained rate constants for the hydroxyl radical experiments (Part II) may be seen in the following tables. The raw data may be seen in Appendix F.

Table 11. Summary of rate reactions for Part II, pH 4

pH 4				
O_3/H_2O_2	$k_{OH\text{-}E1}$ ($M^{-1}s^{-1}$)			
	Replicate 1	**Replicate 2**	**Average**	**Standard deviation**
1:2	2.16×10^{10}	2.64×10^{10}	2.40×10^{10}	3.33×10^{9}
2:1	8.45×10^{10}	5.60×10^{10}	7.03×10^{10}	2.02×10^{10}
4:1	4.58×10^{10}	3.57×10^{10}	4.08×10^{10}	7.19×10^{9}

As seen in Table 11, average rate constants for pH 4 range from 2.40×10^{10} $M^{-1}s^{-1}$ at an O_3/H_2O_2 ratio of 1:2, to 7.03×10^{10} $M^{-1}s^{-1}$ at an O_3/H_2O_2 ratio of 2:1. Standard deviations range from 3.33×10^{9} $M^{-1}s^{-1}$ to 2.02×10^{10} $M^{-1}s^{-1}$.

Table 12. Summary of rate reactions for Part II, pH 7

pH 7				
O_3/H_2O_2	$k_{OH\text{-}E1}$ ($M^{-1}s^{-1}$)			
	Replicate 1	**Replicate 2**	**Average**	**Standard deviation**
1:2	3.32×10^{10}	9.74×10^{9}	2.15×10^{10}	1.66×10^{10}
2:1	9.85×10^{9}	1.30×10^{10}	1.14×10^{10}	2.21×10^{9}
4:1	1.23×10^{10}	1.63×10^{10}	1.43×10^{10}	2.82×10^{9}

As seen in Table 12, average rate constants for pH 7 range from 1.14×10^{10} $M^{-1}s^{-1}$ at an O_3/H_2O_2 ratio of 2:1, to 2.15×10^{10} $M^{-1}s^{-1}$ at an O_3/H_2O_2 ratio of 1:2. Standard deviations range from 2.21×10^9 $M^{-1}s^{-1}$ to 1.66×10^{10} $M^{-1}s^{-1}$.

Table 13. Summary of rate reactions for Part II, pH 8.5

pH 8.5				
O_3/H_2O_2	k_{OH-E1} ($M^{-1}s^{-1}$)			
	Replicate 1	**Replicate 2**	**Average**	**Standard deviation**
1:2	1.27×10^{10}	3.34×10^{10}	2.31×10^{10}	1.47×10^{10}
2:1	1.41×10^{10}	1.67×10^{10}	1.54×10^{10}	1.84×10^{9}
4:1	1.32×10^{10}	2.08×10^{10}	1.70×10^{10}	5.37×10^{9}

As seen in Table 13, average rate constants for pH 8.5 range from 1.54×10^{10} $M^{-1}s^{-1}$ at an O_3/H_2O_2 ratio of 2:1, to 2.31×10^{10} $M^{-1}s^{-1}$ at an O_3/H_2O_2 ratio of 1:2. Standard deviations range from 1.84×10^9 $M^{-1}s^{-1}$ to 1.47×10^{10} $M^{-1}s^{-1}$.

From the above tables, it can again be seen that a definitive O_3/H_2O_2 effect is not present. It may also be seen that the rate reactions are mostly within the same order of magnitude, and that order of magnitude is three orders above the highest reaction rate in Part I (to be discussed later). Also unlike Part I is that a pH effect cannot be easily seen for Part II.

4.2.3. Comparison of rate constants

The results for Parts I and II may be compared with previous reaction rate constant work. A summary of several studies is presented in Table 14.

Table 14. Summary of published rate reaction data

Hormone	Oxidant	k ($M^{-1}s^{-1}$)	Reference
EE2	O_3 ·OH	7×10^9 (pH 6) 9.8×10^9 (pH 7)	Huber et al., 2003
E1	O_3 O_3	2×10^5 (pH 2 to pH 4.5) 5×10^9 (pH 10.5)	Deborde et al., 2005
EE2 E2	·OH ·OH	1.08×10^{10} (pH 6.8) 1.41×10^{10} (pH 6.8)	Rosenfeldt and Linden, 2004

Note: All ·OH values obtained using UV/H_2O_2

As seen in Table 14, previous work also varies across several orders of magnitude. It is also important to note that most of the values reported in Table 14 are for EE2 and E2, not E1. Still, the values reported for ·OH reaction rate constants are in close agreement with those obtained in Part II, being within the same or one order of magnitude. Published results for O_3-E1 reaction rate constants, however, differ from the results obtained here; the difference is two orders of magnitude at the pH 4 range.

4.3. Statistical analysis

As the experimental design was a three level factorial design, using analysis of variance (ANOVA) in Excel to analyze the results would have been unfeasible. Also, as the final experimental results are calculated (i.e., the rate constants), the assumptions necessary for ANOVA may not necessarily be valid. Thus, it was more practical to use linear regression for statistical analysis.

The linear regression tool in Excel was used for analysis, and the inputs were pH, O_3/H_2O_2 ratio and the calculated rate constants. The rate constants used were from those runs that had an r^2 of 0.75 or greater (from original graphs containing intercepts), or best r^2 value obtained for those particular conditions. Parts I and II were analyzed separately.

4.3.1. Statistical analysis for Part I

The initial output for Part I showed extremely large errors and thus was not used further, nor included in this thesis. A log transformation was applied to the calculated rate constants, and the resulting linear regression output was of acceptable quality. It showed the overall data to be significant, and pH to be a significant factor, both at the 95% confidence level. O_3/H_2O_2 ratio was shown to be significant at the 95% confidence level, albeit slightly. A summary of the Excel regression output may be seen in Table 15.

Table 15. Excel regression output for direct ozone-E1 rate constants

Regression Statistics	
Multiple R	1.00
R Square	0.99
Adjusted R Square	0.99
Standard Error	0.15
Observations	19

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	2	42.42	21.21	928.64	2.83E-17
Residual	16	0.37	0.02		
Total	18	42.78			

Parameters	*Coefficients*	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	0.43	0.14	3.16	0.006	0.14	0.72
pH	0.79	0.02	43.08	5.62E-18	0.75	0.83
O_3/H_2O_2	0.05	0.02	2.30	0.04	0.00	0.11

As seen in Table 15, the adjusted r^2 for the direct ozone-E1 rate constants was 0.99, which is quite good. From the significance F, it can be seen that the overall regression is significant. Similarly, it can be seen that the P values for both the intercept and pH are less than α, indicating that those parameters are statistically significant. The P value for O_3/H_2O_2 ratio is marginally less than α, indicating that O_3/H_2O_2 ratio is a statistically significant factor in the direct ozone-E1 rate constant.

Interestingly, the intercept is also statistically significant although it has no experimental basis. One could consider it to represent a sort of "base" value, since, if all other parameters were removed, it would still yield a value for log rate constant. Some might consider it statistical noise or perhaps a sign or by-product of the variability inherent to competitive kinetics. The intercept may perhaps represent an unaccounted-for variable, which may be determined via the residual plots.

While the above mentioned regression yields an acceptable r^2 value, it does have some bias. This bias was apparent in some of the residual plots. Selected residual plots are seen in the following two figures.

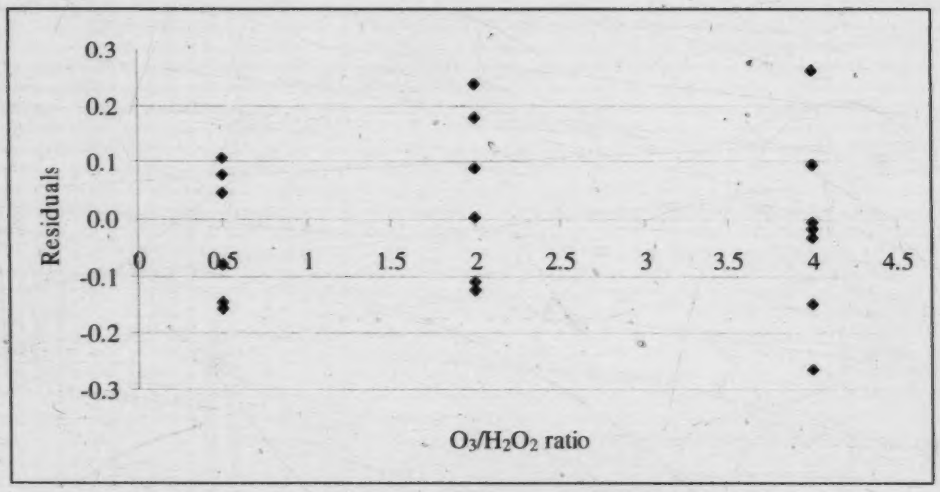


Figure 11. Regression residuals vs. O_3/H_2O_2 ratio (Part I).

As see in Figure 11, the residuals appear to be randomly distributed in terms of O_3/H_2O_2 ratio, indicating that the regression model does not have an apparent bias in terms of O_3/H_2O_2 ratio.

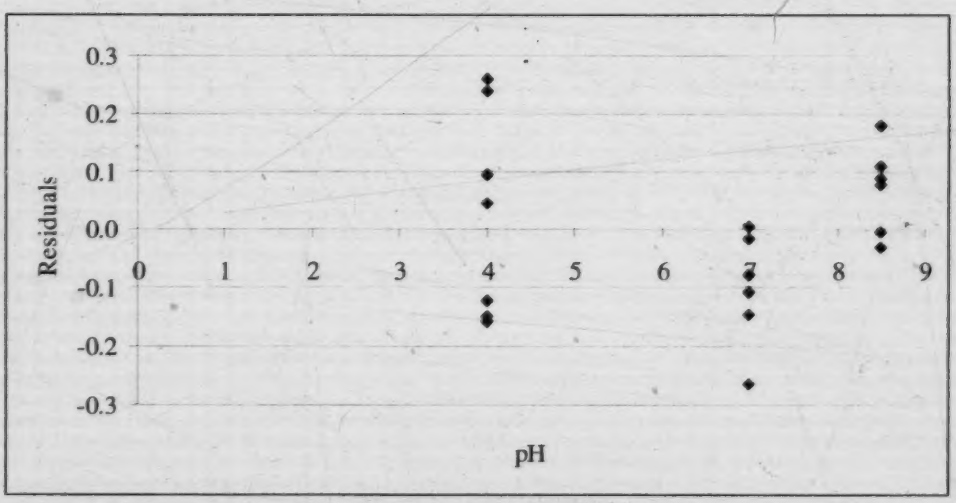


Figure 12. Regression residuals vs. pH (Part I).

From Figure 12, one may see that not all the residuals were randomly distributed. It may be seen in Figure 12 that nearly all of the residuals corresponding with pH 7 are below zero, while many of the residuals corresponding with pH 8.5 are greater than zero. This indicates bias in the regression model, in the form of

under-prediction of rate constants for pH 7 and a possible over-prediction of rate constants for pH 8.5. The exact magnitude of this bias is uncertain at this time.

Alternatively, some may view the residual output seen in Figure 12 as representing a curved band. If this were the case, it would indicate that the model is inadequate and requires higher order terms, a transformation or perhaps another regressor (Montgomery et al., 2000). The case may also be made that without a range of values for x (representing pH), this inference is not valid – there are simply too few data points to form such a pattern.

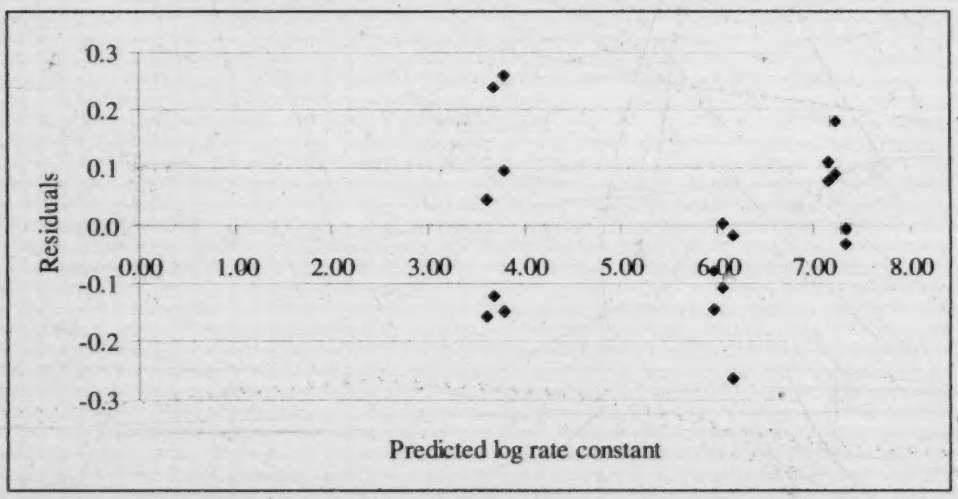


Figure 13. Regression residuals vs. predicted log rate constant (Part I).

Figure 13 shows a trend similar to that seen in Figure 12. A curved band-like trend can be seen. Again, the same implications may be considered, but the large gaps between the various data groups make it difficult to draw a firm conclusion. Interestingly, a graph of obtained log rate constant vs. residuals (not shown in this thesis) was nearly identical to Figure 13 above.

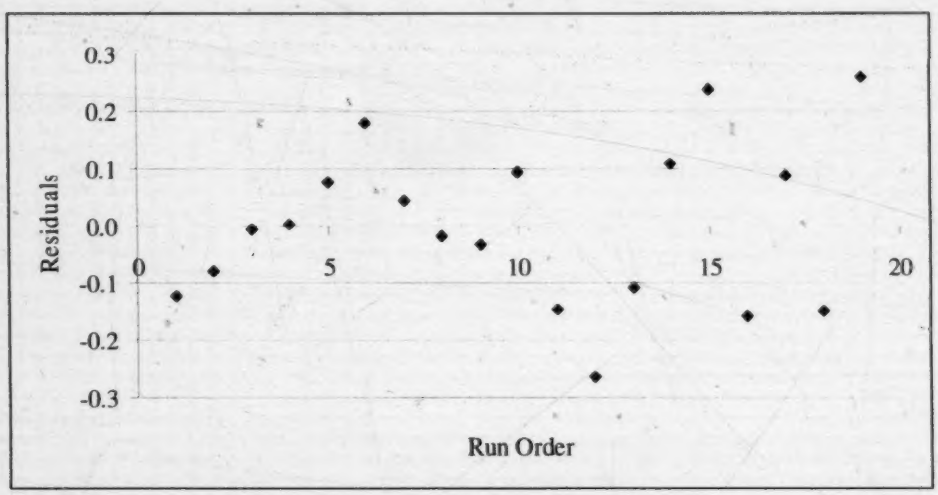


Figure 14. Regression residuals vs. run order (Part I).

Figure 14 shows the regression residuals plotted against run order. As can be seen, the points are randomly distributed. This indicates that a time bias is not likely present. Considering that run order was randomly assigned, this is to be expected.

4.3.2. Statistical analysis for Part II (·OH experiments)

With respect to Part II, both the initial regression output and the log transformed regression output showed large errors. As the log transformed output had a marginally better multiple r^2 value, it was the one used. The Excel regression output may be seen in Table 16.

Table 16. Excel regression output for ·OH-E1 rate constants

Regression Statistics	
Multiple R	0.65
R Square	0.42
Adjusted R Square	0.34
Standard Error	0.22
Observations	18

ANOVA

	df	*SS*	*MS*	*F*	*Significance F*
Regression	2	0.53	0.26	5.43	0.016855
Residual	15	0.73	0.05		
Total	17	1.26			

Parameters	*Coefficients*	*Standard Error*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	10.93	0.20	53.56	1.51E-18	10.49	11.36
pH	-0.09	0.03	-3.29	0.0049	-0.15	-0.03
O_3/H_2O_2	0.00	0.04	0.05	0.9621	-0.08	0.08

As seen in Table 16, the adjusted r^2 for Part II is 0.34, which is quite poor. From the significance F value of 0.017, it can be seen that the overall regression is significant. From the P-values, it can be seen that the intercept and pH are both statistically significant, while O_3/H_2O_2 ratio is not. This is not consistent with the results obtained for Part I, where O_3/H_2O_2 was statistically significant.

One interesting point is that the value for the intercept coefficient, 10.93, greatly exceeds that of the pH coefficient, -0.09. This could be taken to indicate that the inherent noise of the experiments has a larger influence on reaction rate than pH does. Coupled with the adjusted r^2 value, this throws doubt on the value of the data obtained in Part II. Selected residual plots may be seen in the following figures.

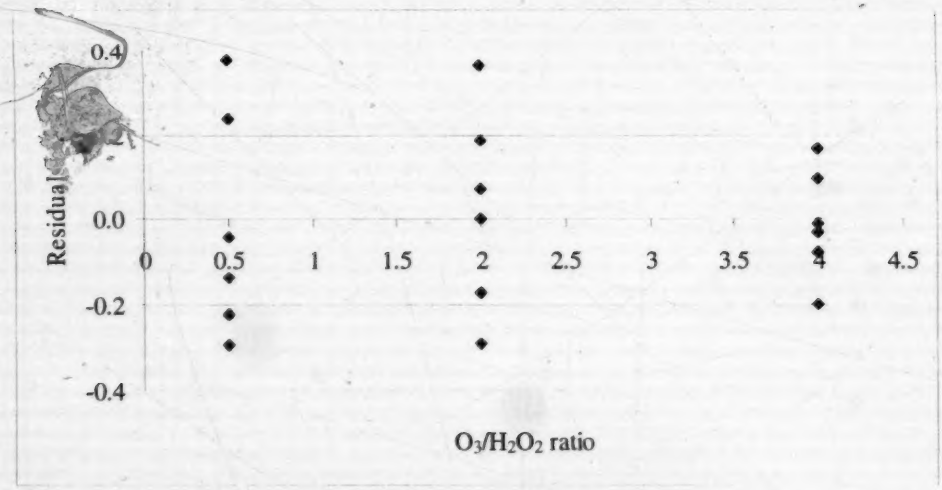


Figure 15. Regression Residuals vs. O_3/H_2O_2 Ratio (Part II).

From Figure 15, it can be seen that there is not really any particular pattern in the distribution of residuals vs. O_3/H_2O_2 ratio; the residuals appear to be randomly distributed. Since O_3/H_2O_2 ratio is not statistically significant for these experiments, it would be extremely odd to see any sort of pattern in these residuals.

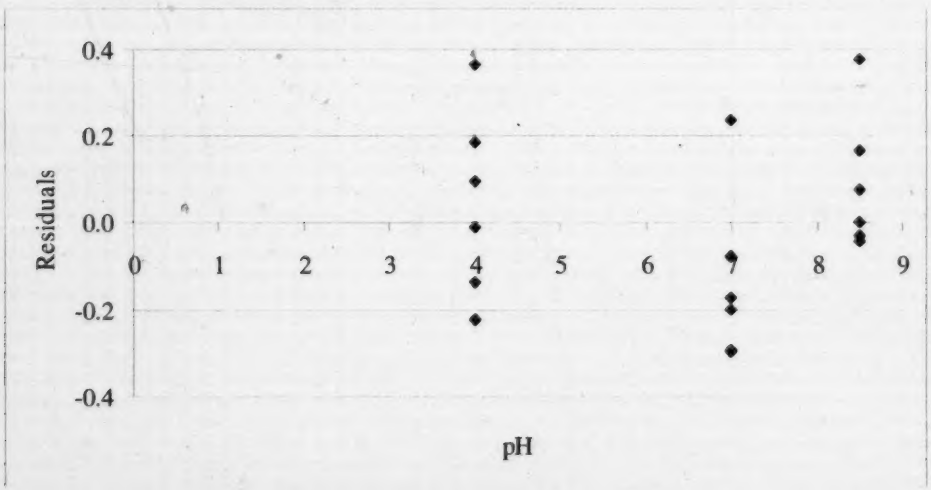


Figure 16. Regression residuals vs. pH (Part II).

From Figure 16, it is apparent that there is no particular pattern in the regression residuals plotted against pH. The regression model does not appear to over or under-predict the log

transformed rate constant. Again, plotting the residuals versus the set experimental factors gives an indication of whether the regression model displays bias in terms of the experimental factors. Without a continuum of set experimental factors, however, it may not be possible to draw conclusions regarding the model adequacy.

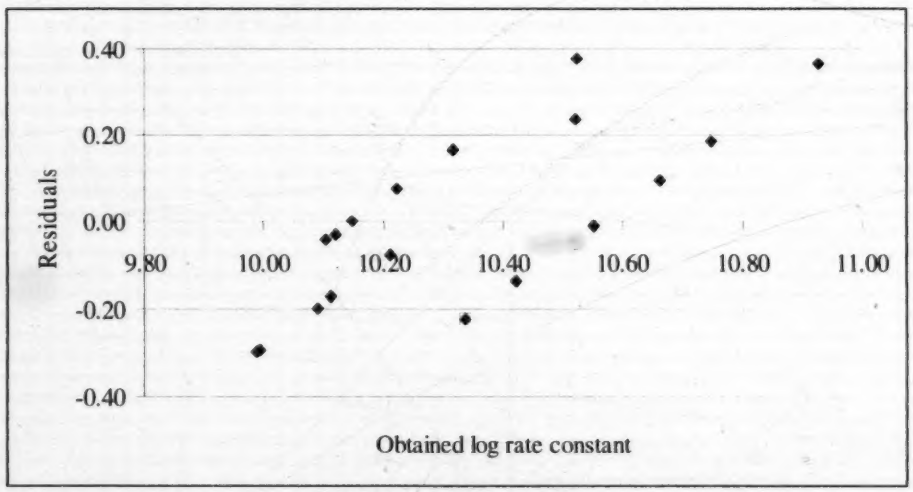


Figure 17. Regression residuals vs. log transformed rate constant (Part II).

From Figure 17, a very slight trend may be seen with increasing log transformed rate constant. After 10.60, all the residuals are positive, indicating perhaps an over-prediction of the rate constant after that point.

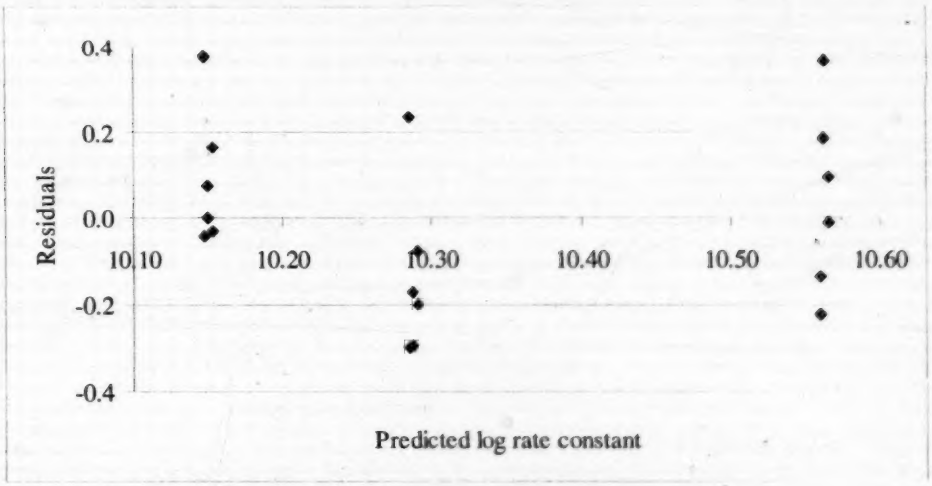


Figure 18. Regression residuals vs. predicted log transformed rate constant (Part II).

Examining the residuals pattern in Figure 18, a slight curved band effect can be seen. This indicates, as noted before, model inadequacy. There are several possible reasons for this effect: a higher order term is required, a transformation of the x or y is required, or another regressor should be considered (Montgomery et al., 2000).

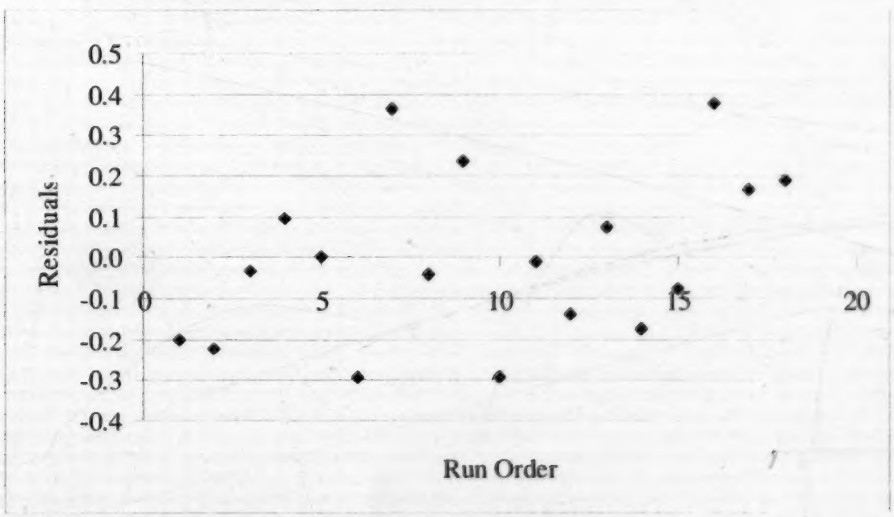


Figure 19. Regression residuals vs. run order (Part II).

The concerns raised by Figure 18 are somewhat mollified by Figure 19. Figure 19 shows a random distribution of residuals against run order, indicating that there is not a run order bias, and that run order is not likely an unaccounted for regressor.

Overall, it can be concluded that pH is a significant parameter in O_3/H_2O_2 treatment. It can also be concluded that pH has a much greater effect on the direct ozone pathway than the indirect (i.e., ·OH pathway). The values of the pH and intercept coefficient were 0.79 and 0.94 respectively, for the direct ozone experiments, and -0.09 and 10.93 respectively for the ·OH experiment. The value of the O_3/H_2O_2 ratio coefficient was 0.05 for Part II and 0 for Part II.

The direct ozone pH coefficient not only had a greater magnitude than that of the Part II experiments, but was also much closer in value to the direct ozone intercept coefficient. This indicates reasonable parity in the significance of these parameters in the Part I experiments.

The discrepancy between the Part II pH and intercept coefficients (an order of magnitude) indicate that those two parameters have effects of greatly differing magnitude. In light of the residuals seen for Part II, the possibility of the intercept representing an unaccounted-for factor must be considered. On the other hand, pH was not expected to play as large a role in the Part II experiments as in Part I. Hydroxyl radicals are not considered to be as influenced by pH as ozone is. It is possible that this lesser value for pH coefficient in Part II is more reflective of E1's behaviour under varying pH conditions than the behaviour of the oxidant. That being said, only limited conclusions may be drawn regarding Part II owing to the poor quality of the data.

It is rather surprising that O_3/H_2O_2 ratio was not found to be more statistically significant in Part I, or statistically significant at all in Part II. Theoretically, O_3/H_2O_2 ratio should be important, both because of the inhibitory/promoter effect of H_2O_2 in ozone auto-decomposition, and the effect of H_2O_2 seen in some O_3/H_2O_2 experiments. It has been observed that, in some O_3/H_2O_2 experiments. degradation diminishes or slows as a critical H_2O_2 concentration is reached (Beltrán, 2004). This is thought to be a symptom of H_2O_2 starting to inhibit ozone decomposition (Beltrán, 2004).

It may be that this critical H_2O_2 concentration effect was not seen because the contaminants, not the oxidants, were in excess. It is

believed, that for the situations mentioned above, the studies were conducted as conventional percent degradation studies, and thus the oxidants were in excess. In competitive kinetics, the contaminants are in excess. Perhaps the contaminant-oxidant reaction in these experiments is occurring before H_2O_2 can inhibit ozone auto-decomposition, or ozone is consumed before a significant amount of auto-decomposition can occur. It may be possible that O_3/H_2O_2 ratio has no influence over reaction rate per se, but may influence total contaminant removal or transformation.

4.4. Experimental issues

It has been recognized that competitive kinetics has a larger degree of error associated with it than direct rate measurement. As previously noted, however, direct rate measurement is simply not feasible in most situations for experiments where the expected rate of reaction is very fast. In addition to the analytical error possible, competitive kinetics must also deal with the possibility of error in the reported rate of reaction between the oxidant of interest and the reference compound. Thus, there is bound to be great variability in results obtained by competitive kinetics, as evidenced by the data presented.

Another striking experimental issue is the group of assumptions necessary for determining the ·OH-E1 rate constant. The inherent assumption in using this method is that E1 is reacting primarily with hydroxyl radicals. In reality, both hydroxyl radical and direct –ozone E1 reactions will occur. The practice of not having a scavenger for hydroxyl radical rate constant determination is realistic for the contaminants previously tested in the literature by this method, as they had been demonstrated to react very slowly with ozone (Acero et al., 2000). Questions will arise over using this method for a contaminant that is known to react strongly with ozone, and indeed the approach used is not entirely rigourous. One cannot say that all the observed E1 reduction is due to ·OH reaction alone; some has to be occurring due to O_3 oxidation. Thus, the rate constants presented for the ·OH-E1 reaction are really rate constants for the overall O_3/H_2O_2-E1 reaction, rate constants that encompass both direct and indirect ozone reactions, plus the influence of H_2O_2.

That being said, it is still possible to interpolate ·OH-E1 rate constants from the data. The data obtained in Part II is essentially O_3 + ·OH; the data obtained in Part I gives us O_3. By subtracting the rate constant obtained in Part I for each experimental setting, from the rate constant

obtained in Part II for the same setting, an apparent ·OH-E1 rate constant may be found. These rate constants may be seen in the following table.

Table 17. Obtained and apparent ·OH-E1 rate constants.

Setting		k ($M^{-1}s^{-1}$)		
pH	O_3/H_2O_2	Part I - O_3	Part II - O_3 + ·OH	Apparent ·OH
4	1:2	3.65×10^3	2.40×10^{10}	2.40×10^{10}
	2:1	6.07×10^3	7.03×10^{10}	7.03×10^{10}
	4:1	7.93×10^3	4.08×10^{10}	4.08×10^{10}
7	1:2	7.19×10^5	2.15×10^{10}	2.15×10^{10}
	2:1	1.00×10^6	1.14×10^{10}	1.14×10^{10}
	4:1	1.09×10^6	1.43×10^{10}	1.43×10^{10}
8.5	1:2	1.74×10^7	2.31×10^{10}	2.31×10^{10}
	2:1	2.32×10^7	1.54×10^{10}	1.54×10^{10}
	4:1	2.1×10^7	1.70×10^{10}	1.70×10^{10}

As seen in Table 17, there is little difference between the obtained and apparent ·OH rate constants. This is due to the fact that the ·OH-E1 rate constants are at least three orders of magnitude larger than the O_3-E1 rate constants; subtracting the O_3-E1 rate constants will not make an appreciable difference as far as significant figures go.

While this approach may not seem entirely valid, such may not necessarily be the case. For the reaction of E1 with ozone, the rate law is commonly expressed as follows:

$$-r_{E1} = zk_D C_{O3} C_{E1} + k_{OH-E1} C_{OH} C_{E1}$$

It can be seen that the overall reaction rate (r) is already comprised of components representing the consumption of E1 by direct ozone and the consumption of E1 by hydroxyl radicals. From a very basic standpoint, the rate constants obtained in this experiment for Part II are indeed comprised of both direct ozone and hydroxyl radical mechanisms. Granted, the relationship may not be 1:1 and as such the apparent rate constants must be viewed as an approximation.

Some may also contend that such an approach is overly simplistic, that it ignores the role of other radicals present during ozone decomposition and that overall contaminant removal in an ozone-based treatment system cannot be reduced to merely the sum of direct ozone and hydroxyl radical reactions. While this is true in a rigorous, theoretical sense, it is not true in a practical sense. There are a number of proposed ozone decomposition mechanisms, each with its own particular merits. Using a different mechanism will yield different results. Moreover, it may be next to impossible to determine the presence and effect of the

various radicals; some are short-lived and intermediate. Thus, for practicality's sake, discussion of ozone treatment is limited to consideration of direct ozone and hydroxyl radical mechanisms, as has been the case for most ozone kinetics work to date (as seen in Section 2).

Another strong point of contention is that of using competitive kinetics in an ozone system to determine the hydroxyl radical rate of reaction for a contaminant that also reacts strongly with ozone, mentioned previously. As shown in Section 2, UV/H_2O_2 is commonly used for such a purpose, as it would be impossible to block direct ozone action in an ozone treatment system. On a theoretical basis, an approach such as that shown in Part II is only advised if the contaminant's reaction with ozone is negligible; in order for the competitive kinetics relationship to be valid, either the direct ozone mechanism or the hydroxyl radical mechanism must cancel out. In Part I, this was ensured through the use of a hydroxyl radical scavenger to block hydroxyl radical degradation. There was no such scavenger in Part II. However, since there is a minimum of three orders of magnitude difference between the E1-ozone reaction rate and the E1-hydroxyl radical reaction rate, the direct ozone-E1 reaction is *practically* negligible compared to the hydroxyl radical-E1 reaction. Thus, Part II may not be theoretically rigorous in its basis, but it is defensible on a practical basis.

4.5. Error analysis

In addition to the experimental issues discussed previously, it is important to consider the various potential sources of errors in this work. The main areas of errors are experimental execution, experimental method and theoretical basis.

With regards to experimental execution, several sources of errors exist. A large potential source of errors would the HPLC system. The HPLC system only possessed one pump, which could be responsible for baseline drift. Also, the HPLC system was in great need of servicing by the end of Part II experiments; scans were very noisy and thus peak area counts may have been overestimated.

Another source of experimental execution error could be the E1 stock. The E1 stock was filtered and it is possible that the filter size used was large enough to allow some solids to pass through. Although the stock solution was kept constantly stirring to ensure homogeneity, the solution was not likely to be 100% homogeneous. Moreover, any solid particles could have thrown the results off.

For experimental method, it is likely that Part I data was of such a good quality because the reference compound used in Part I (phenol) is so similar to E1. Thus, the contaminant and reference compound behaved in a similar fashion. Likewise, the poor quality data of Part II may partly be a result of the many structural differences between acetophenone and E1. In the future, it may be beneficial to choose a reference compound for Part II-style work that is more similar to E1. It has also been noted that the method of competitive kinetics itself is prone to errors; the accuracy of the obtained rate constants is only as good as the accuracy of the reference compound's rate constant (Beltrán, 2004).

On a theoretical basis, the main source of errors would be using the approach of Part II. As noted above, using competitive kinetics to determine hydroxyl radical rate reactions in an ozone-based treatment system, with a contaminant that reacts strongly with ozone, is not supported on a theoretical basis. This may be another cause of the poor quality of data obtained in Part II.

5. Conclusions and recommendations

As discussed previously, eEDCs have been demonstrated to be environmentally prevalent. Concern has been raised over the fact that human and environmental health are potentially being threatened by environmental concentrations of estrogenic EDCs. Moreover, EDC fate and observational studies have shown that conventional water and wastewater treatment processes may be inadequate to fully remove EDCs from effluent. It is also difficult to predict EDC removal in conventional treatment plants.

From the previous literature review, it can be seen that ozone-based AOPs offer great promise in treating steroidal estrogens. The highest level of treatment was seen with those AOPs that involved ozone.

For the experiments described in this thesis, it was found for the direct ozone-E1 reaction (Part I) that rate constants ranged between 3.65×10^3 $M^{-1}s^{-1}$ at pH 4, O_3/H_2O_2 = 1:2, and 2.32×10^7 $M^{-1}s^{-1}$ at pH 8.5, O_3/H_2O_2 = 2:1. By far, pH had the greatest influence on rate reaction, whereas O_3/H_2O_2 ratio was found to be slightly statistically significant.

For the hydroxyl radical-E1 reaction (Part II), apparent rate constants ranged between 1.14×10^{10} $M^{-1}s^{-1}$ at pH 7, O_3/H_2O_2 = 2:1, and 7.03×10^{10} $M^{-1}s^{-1}$ at pH 4, O_3/H_2O_2 = 2:1. Again, pH was statistically significant but O_3/H_2O_2 ratio was not. The regression output for this group of experiments showed considerable noise and the possibility of an unknown regressor.

Overall, both sets of experiments yielded results that are generally in line with published work, both for E1 and other estrogens. O_3/H_2O_2 treatment is effective for E1, as evidenced by the rapid reaction rates. At this time, however, the role of O_3/H_2O_2 ratio remains uncertain.

For future work, quality of data could be ensured by a better quality analytical system. Using LC/MS rather HPLC for quantification may reduce data variability. Moreover, using a different reference compound to determine hydroxyl radical rate constants would likely yield data of much better quality than that seen for Part II.

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7. Appendices

Appendix A: Standards and stock analysis

Appendix B: HPLC run results, Part I (direct O_3 experiments)

Appendix C: Rate constant sample calculations and results, Part I (direct O_3 experiments)

Appendix D: HPLC standards and method description, Part II (·OH experiments)

Appendix E: HPLC run results, Part II (·OH experiments)

Appendix F: Rate constant sample calculations and results, Part II (·OH experiments)

Appendix A: Standards and Stock Analysis

Shimadzu HPLC unit

HPLC Method Description (Direct Ozone Rate Reaction Experiments)

Gradient: isocratic, 60% acetonitrile, 40% Elga water (both filtered)
Column: C18 5 µm Phenomenex column, 250 mm ×4.6 mm Injection volume: 20 µL
Run time: 15 min.

Standards done between Oct. 5 and Oct. 6th, 2006.

Table 7.1. E1 Standards and HPLC Analysis (Part I)

Concentration	Replicate	Peak Area	Retention Time (min.)	Standard Deviation*
5 µM	1	11714	7.3	493.0
	2	10765	7.3	
	3	11471	7.3	
	Average	**11317**	**7.3**	
3.5 µM	1	9005	7.317	861.8
	2	8638	7.283	
	3	7363	7.3	
	Average	**8335**	**7.300**	
2 µM	1	4776	7.3	402.4
	2	5015	7.3	
	3	4230	7.317	
	Average	**4674**	**7.306**	
1 µM	1	2467	7.3	142.9
	2	2191	7.283	
	3	2265	7.317	
	Average	**2308**	**7.300**	

* Standard deviation calculated using peak area counts.

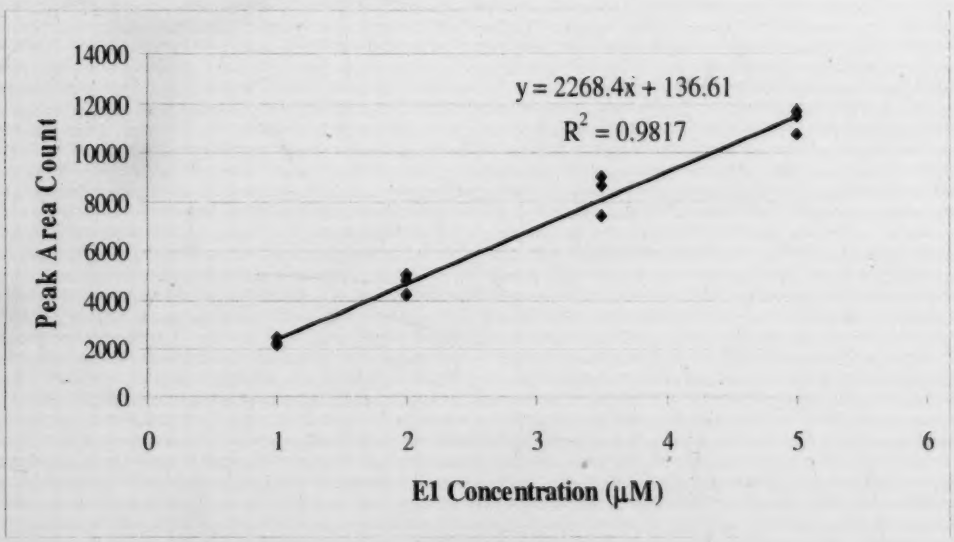

Figure 7.1. E1 Concentration Standard Curve (Part I)

Standards done on Oct. 6 and Oct. 10th, 2006

HPLC Method Description

Same as that for E1

Table 7.2. Phenol Standard (Part I)

Concentration	Replicate	Peak Area	Retention Time (min.)	Standard Deviation*
5 µM	1	10182	4.283	801.4
	2	10917	4.3	
	3	9316	4.283	
	Average	**10138**	**4.289**	
3.5 µM	1	6336	4.283	337.0
	2	6479	4.283	
	3	6978	4.3	
	Average	**6598**	**4.289**	
2.5 µM	1	4976	4.317	114.8
	2	5143	4.333	
	3	4923	4.317	
	Average	**5014**	**4.322**	
1 µM	1	1901	4.3	89.8
	2	1916	4.283	
	3	2028	4.317	
	Average	**1948**	**4.300**	

* Standard Deviation calculated in terms of peak area counts.

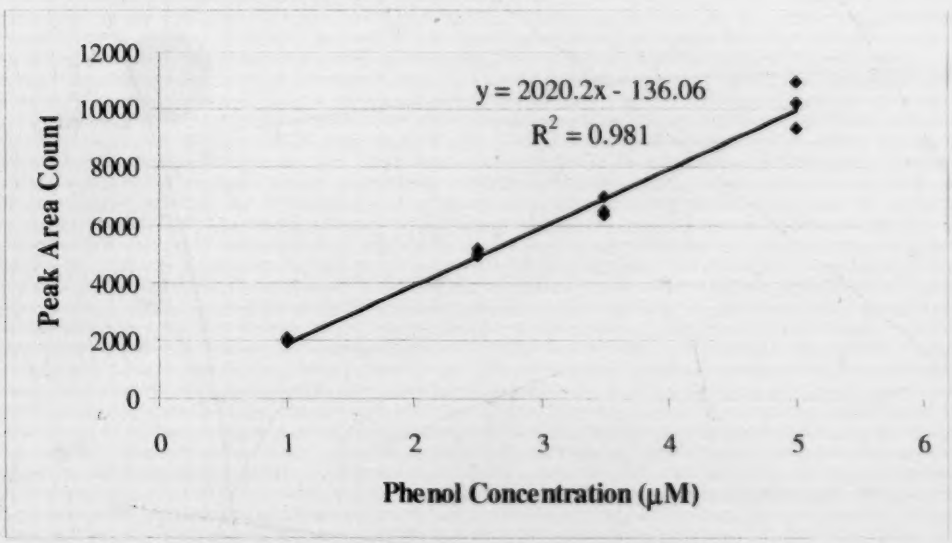

Figure 7.2. Phenol Standard Curve (Part I)

E1 Stock Analysis

First Batch (Part I)

PAC	E1 Concentration (μM)
10336	4.50
10465	4.55
8778	3.81
12278	5.35
Average	4.55
Standard Deviation	0.63

Second Batch (Part I) [redacted]

PAC	E1 Concentration (μM)
3625	3.08
3394	2.87
[redacted]	
3660	3.11
4360	3.72
Average	3.19
Standard Deviation	0.37

First Batch (Part II)

PAC	E1 Concentration (μM)
2943	2.57
2861	2.50
2908	2.54
Average	2.54
Standard Deviation	0.03
% Difference	1.30

Second Batch (Part II)

PAC	E1 Concentration (μM)
7961	6.58
8388	6.92
7698	6.37
Average	6.624
Standard Deviation	0.28
% Difference	4.20

Oxidant Stock Calculations

Part I

O_3/H_2O_2 = 2:1				
	Final Dose (μM)	**Stock Needed (μM)**		
H_2O_2	5	100		
	3.75	75		
	2.5	50		
	1.25	25	**Concentration (mg/L)**	**Absorbance (AU)**
O_3	10	200	9.60	0.662
	7.5	150	7.20	0.497
	5	100	4.80	0.331
	2.5	50	2.40	0.166

O_3/H_2O_2 = 4:1				
	Final Dose (μM)	**Stock Needed (μM)**		
H_2O_2	3	60		
	2	40		
	1	20		
	0.5	10	**Concentration (mg/L)**	**Absorbance (AU)**
O_3	12	240	11.52	0.794
	8	160	7.68	0.530
	4	80	3.84	0.265
	2	40	1.92	0.132

O_3/H_2O_2 = 1:2				
	Final Dose (μM)	**Stock Needed (μM)**		
H_2O_2	10	200		
	7.5	150		
	5	100		
	2.5	50	**Concentration (mg/L)**	**Absorbance (AU)**
O_3	5	100	4.80	0.331
	3.75	75	3.60	0.248
	2.5	50	2.40	0.166
	1.25	25	1.20	0.083

Part II

O_3/H_2O_2 = 2:1				
	Final Dose (μM)	**Stock Needed (μM)**		
H_2O_2	2.5	50		
	1.875	37.5		
	1.25	25		
	0.625	12.5	**Concentration (mg/L)**	**Absorbance (AU)**
O_3	5	100	4.80	0.331
	3.75	75	3.60	0.248
	2.5	50	2.40	0.166
	1.25	25	1.20	0.083

O_3/H_2O_2 = 4:1				
	Final Dose (μM)	**Stock Needed (μM)**		
H_2O_2	1.5	30		
	1	20		
	0.5	10		
	0.25	5	**Concentration (mg/L)**	**Absorbance (AU)**
O_3	6	120	5.76	0.397
	4	80	3.84	0.265
	2	40	1.92	0.132
	1	20	0.96	0.066

O_3/H_2O_2 = 1:2				
	Final Dose (μM)	**Stock Needed (μM)**		
H_2O_2	5	100		
	3.75	75		
	2.5	50		
	1.25	25	**Concentration (mg/L)**	**Absorbance (AU)**
O_3	2.5	50	2.40	0.166
	1.875	37.5	1.80	0.124
	1.25	25	1.20	0.083
	0.625	12.5	0.60	0.041

Appendix B: HPLC run results, Part I (direct O_3 experiments)

All runs conducted at ambient temperatures between 19.3°C and 20.8°C

Table 7.3. Part I - Replicate 1, Run 1 Phenol Results: pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
				Phenol			
Control	3	3012	5.15	3.12	3.07	0.06	[redacted]
	4	2982	5.133	3.09			
	5	2892	5.25	3.00			
1	3	3425	5.15	3.53	2.68	0.74	[redacted]
	4	2217	5.15	2.33			
	5	2073	5.133	2.19			
2	3	2658	5.15	2.77	2.56	0.20	[redacted]
	4	2440	5.15	2.55			
	5	2256	5.233	2.37			
3	3	2343	5.15	2.45	2.48	0.14	[redacted]
	4	2231	5.133	2.34			
	5	2521	5.25	2.63			
4	3	2428	5.15	2.54	2.83	0.26	[redacted]
	4	2933	5.133	3.04			
	5	2800	5.25	2.91			

Table 7.4. Part I - Replicate 1, Run 1 E1 Results: pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
				E1			
Control	3	4152	11.683	3.54	3.52	0.13	[redacted]
	4	4258	11.667	3.63			
	5	3960	12.417	3.37			
1	3	3673	11.7	3.12	2.34	0.68	[redacted]
	4	2496	11.683	2.08			
	5	2206	11.667	1.82			
2	3	2223	11.7	1.84	2.01	0.26	[redacted]
	4	2759	11.683	2.31			
	5	2271	12.4	1.88			
3	3	2699	11.683	2.26	2.28	0.26	[redacted]
	4	2450	11.65	2.04			
	5	3028	12.4	2.55			
4	3	3323	11.7	2.81	3.01	0.27	[redacted]
	4	3909	11.667	3.33			
	5	3431	12.417	2.90			

Table 7.5. Part I - Replicate 1, Run 1 Excluded Results: pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Phenol							
Control	1 2	2421 2548	4.317 4.633	2.53 2.66	2.77	0.31	[redacted]
1	1 2	1111 1453	4.317 4.317	1.23 1.57	2.11	1.24	[redacted]
2	1 2	1305 1144	4.317 4.233	1.43 1.27	1.82	0.82	[redacted]
3	1 2	1848 1601	4.317 4.35	1.96 1.72	2.05	0.37	[redacted]
4	1 2	1676 1918	4.317 4.633	1.79 2.03	2.12	0.38	[redacted]
E1							
Control	1 2	3388 3764	7.45 8.9	2.87 3.20	3.20	0.34	[redacted]
1	1 2	2101 2082	7.45 7.433	1.73 1.72	2.19	0.81	[redacted]
2	1 2	2566 2323	7.433 7.117	2.14 1.93	1.97	0.16	[redacted]
3	1 2	3024 2784	7.433 8.333	2.55 2.33	2.38	0.15	[redacted]
4	1 2	2808 2915	7.417 8.9	2.36 2.45	2.54	0.24	[redacted]

*Data was excluded from calculations – elution scheme was changed, yielding varying results.

Table 7.6. Part I - Replicate 1, Run 1.2 Phenol Results: pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1074	8.117	1.20	1.54	0.26	16.86
	2	1349	8.017	1.47			
	3	1586	8	1.70			
	4	1650	7.983	1.77			
1	1	1089	8.133	1.21	1.06	0.17	16.02
	2	1057	8.117	1.18			
	3	737	8	0.86			
	4	836	7.967	0.96			
2	1	735	8.1	0.86	1.01	0.11	10.49
	2	980	8.1	1.10			
	3	939	8	1.06			
	4	886	8.017	1.01			
3	1	875	8.117	1.00	1.28	0.23	17.93
	2	1355	8.033	1.48			
	3	1061	8.017	1.19			
	4	1340	8	1.46			
4	1	1320	8.117	1.44	1.30	0.18	13.71
	2	1065	8	1.19			
	3	977	7.983	1.10			
	4	1331	7.967	1.45			

Table 7.7. Part I - Replicate 1, Run 1.2 E1 Results: pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1878	15.033	1.54	1.71	0.27	15.74
	2	1755	14.967	1.43			
	3	2399	14.967	1.99			
	4	2254	14.967	1.87			
1	1	973	15.033	0.74	0.65	0.15	22.63
	2	1045	15.05	0.80			
	3	768	14.967	0.56			
	4	694	14.95	0.49			
2	1	1072	15.033	0.82	0.82	0.05	5.53
	2	1053	15.05	0.81			
	3	1127	14.967	0.87			
	4	1003	14.983	0.76			
3	1	1217	15.033	0.95	0.97	0.09	9.06
	2	1175	14.967	0.92			
	3	1170	14.967	0.91			
	4	1382	14.967	1.10			
4	1	1263	15.033	0.99	1.16	0.16	14.13
	2	1405	14.967	1.12			
	3	1423	14.967	1.13			
	4	1706	14.967	1.38			

Table 7.8. Part I - Replicate 1, Run 1.3 Phenol Results: pH 7, $O_3/H_2O_2 = 2:1$

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1122	7.967	1.25	1.39	0.27	19.80
	2	1090	8.05	1.21			
	3	1586	8.033	1.70			
	4	1242	8.033	1.36			
1	1	728	7.833	0.86	0.74	0.24	31.71
	2	822	8.05	0.95			
	3	633	8.067	0.76			
	4	277	8.033	0.41			
2	1	1314	8.05	1.44	1.19	0.23	19.08
	2	1192	8.067	1.31			
	3	897	8.05	1.02			
	4	841	8.033	0.97			
3	1	1681	8.05	1.80	1.60	0.29	18.09
	2	1777	8.05	1.89			
	3	1255	8.033	1.38			
	4	1203	8.033	1.33			
4	1	1758	8.033	1.88	1.32	0.38	29.22
	2	924	8.033	1.05			
	3	1132	8.033	1.26			
	4	955	8.05	1.08			

Table 7.9. Part I - Replicate 1, Run 1.3 E1 Results: pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	2432	14.95	2.02	1.85	0.25	13.51
	2	1911	14.967	1.56			
	3	2366	14.967	1.97			
	4	2330	14.967	1.93			
1	1	886	14.9	0.66	0.67	0.14	21.12
	2	1126	14.967	0.87			
	3	786	14.983	0.57			
	4	786	14.95	0.57			
2	1	1238	14.95	0.97	0.82	0.16	19.07
	2	1195	14.983	0.93			
	3	972	14.967	0.74			
	4	867	14.95	0.64			
3	1	1600	14.967	1.29	1.24	0.19	15.48
	2	1821	14.967	1.49			
	3	1376	14.967	1.09			
	4	1361	14.95	1.08			
4	1	2467	14.95	2.05	1.50	0.37	24.73
	2	1594	14.967	1.28			
	3	1613	14.95	1.30			
	4	1679	14.967	1.36			

Table 7.10. Part I - Replicate 1, Run 1.4 Phenol Results: pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1479	8.083	1.60	1.64	0.06	3.83
	2	1569	8.083	1.69			
1	1	1078	8.117	1.20	1.13	0.07	6.66
	2	1052	8.083	1.18			
	3	926	8.083	1.05			
	4	946	8.083	1.07			
2	1	1260	8.117	1.38	1.31	0.14	10.37
	2	1035	8.1	1.16			
	3	1340	8.083	1.46			
	4	1118	8.083	1.24			
3	1	1256	8.117	1.38	1.35	0.19	13.90
	2	1016	8.1	1.14			
	3	1474	8.083	1.59			
	4	1181	8.083	1.30			
4	1	1339	8.083	1.46	1.59	0.12	7.27
	2	1416	8.083	1.54			
	3	1582	8.083	1.70			
	4	1563	8.083	1.68			

Table 7.11. Part I - Replicate 1, Run 1.4 E1 Results: pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	3280	15.033	2.77	2.82	0.07	2.61
	2	3398	15.033	2.88			
1	1	1808	15.033	1.47	1.35	0.09	6.29
	2	1666	15.017	1.35			
	3	1635	15.017	1.32			
	4	1582	15.033	1.27			
2	1	2214	15.033	1.83	1.71	0.16	9.27
	2	1834	15.033	1.50			
	3	2210	15.017	1.83			
	4	2041	15.017	1.68			
3	1	2264	15.05	1.88	1.92	0.14	7.43
	2	2113	15.033	1.74			
	3	2451	15.017	2.04			
	4	2445	15.017	2.04			
4	1	2520	15.033	2.10	2.17	0.22	10.22
	2	2284	15.033	1.89			
	3	2757	15.033	2.31			
	4	2844	15.017	2.39			

Table 7.12. Part I - Replicate 1, Run 2 Results: pH 8.5, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Phenol							
Control	1	2421	4.633	2.53	2.78	0.41	14.80
	2	2447	5.15	2.56			
	3	3154	5.267	3.26			
1	1	2373	4.633	2.48	2.39	0.20	8.42
	2	2041	4.633	2.16			
	3	2409	5.25	2.52			
2	1	2373	4.633	2.48	2.64	0.22	8.35
	2	2440	5.117	2.55			
	3	2788	5.25	2.89			
3	1	2440	4.633	2.55	3.01	0.43	14.33
	2	2973	5.133	3.08			
	3	3304	5.25	3.41			
4	1	2307	4.633	2.42	2.56	0.12	4.69
	2	2509	5.133	2.62			
	3	2524	5.25	2.63			
E1							
Control	1	3761	8.883	3.20	3.22	0.28	8.63
	2	3483	11.717	2.95			
	3	4111	12.417	3.50			
1	1	2480	8.883	2.07	1.98	0.18	9.09
	2	2508	8.867	2.09			
	3	2142	12.417	1.77			
2	1	3072	8.883	2.59	2.56	0.31	12.24
	2	2667	11.667	2.23			
	3	3375	12.417	2.86			
3	1	2981	8.867	2.51	2.54	0.18	7.05
	2	2827	11.7	2.37			
	3	3229	12.417	2.73			
4	1	3785	8.867	3.22	2.89	0.29	10.02
	2	3295	11.7	2.78			
	3	3161	12.417	2.67			

Table 7.13. Part I - Replicate 1, Run 2.2 Phenol Results: pH 8.5, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1978	7.917	2.09	1.78	0.24	13.70
	2	1574	7.867	1.69			
	3	1392	7.867	1.51			
	4	1694	7.7	1.81			
1	1	527	7.8	0.66	0.77	0.09	11.62
	2	645	7.883	0.77			
	3	658	7.867	0.79			
	4	748	7.867	0.88			
2	1	861	7.883	0.99	1.15	0.20	
	2	1255	7.9	1.38			
	3	968	7.85	1.09			
	4	879	7.65	1.00	1.07	0.05	4.97
	5	975	7.717	1.10			
3	1	960	7.883	1.09	1.07	0.10	
	2	1041	7.9	1.17			
	3	843	7.883	0.97			
	4	1255	7.717	1.38	1.26	0.26	20.31
	5	1436	7.7	1.56			
	6	1028	7.75	1.15			
4	1	1247	7.917	1.37	1.40	0.03	1.95
	2	1302	7.883	1.42			
	3	1274	7.867	1.40			

Denotes results excluded from calculations – numbered caps were accidentally switched for samples 2 and 3 – results obtained before switch was discovered, were discarded.

Table 7.14. Part I - Replicate 1, Run 2.2 E1 Results: pH 8.5, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	3306	14.85	2.79	2.14	0.44	20.44
	2	2241	14.817	1.86			
	3	2420	14.817	2.01			
	4	2307	14.667	1.91			
1	1	767	14.8	0.56	0.63	0.18	29.55
	2	1134	14.833	0.88			
	3	639	14.817	0.44			
	4	846	14.817	0.63			
2	1	1170	14.833	0.91	1.01	0.10	
	2	1399	14.833	1.11			
	3	1276	14.817	1.00			
	4	1300	14.65	1.03	1.02	0.01	1.15
	5	1298	14.667	1.02			
3	1	1445	14.833	1.15	1.02	0.22	
	/ 2	1007	14.833	0.77			
	3	1445	14.817	1.15			
	4	1268	14.667	1.00	1.03	0.25	24.22
	5	1568	14.667	1.26			
	6	920	14.683	0.69			
4	1	1684	14.833	1.36	1.39	0.03	1.91
	2	1740	14.833	1.41			
	3	1732	14.833	1.41			

Denotes results excluded from calculations– numbered caps were accidentally switched for samples 2 and 3 – results obtained before switch was discovered, were discarded.

Table 7.15. Part I - Replicate 1, Run 3 Results: pH 7, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Phenol							
Control	1	2292	5.1	2.40	2.50	0.18	7.37
	2	2277	5.1	2.39			
	3	2607	5.25	2.72			
1	1	2014	5.067	2.13	1.71	0.42	24.69
	2	1591	5.1	1.71			
	3	1162	5.017	1.29			
2	1	2283	5.083	2.39	2.29	0.09	3.93
	2	2155	5.083	2.27			
	3	2107	5.233	2.22			
3	1	2104	5.083	2.22	2.20	0.12	5.51
	2	1957	5.083	2.07			
	3	2200	5.233	2.31			
4	1	2697	5.1	2.80	2.64	0.16	5.99
	2	2378	5.1	2.49			
	3	2519	5.233	2.63			
E1							
Control	1	2910	11.417	2.45	2.69	0.24	8.94
	2	3188	11.383	2.69			
	3	3455	12.333	2.93			
1	1	1418	11.4	1.13	1.00	0.18	17.67
	2	1340	11.4	1.06			
	3	1040	11.383	0.80			
2	1	2117	11.417	1.75	1.62	0.11	7.03
	2	1951	11.4	1.60			
	3	1862	12.317	1.52			
3	1	2696	11.417	2.26	2.16	0.14	6.34
	2	2410	11.4	2.00			
	3	2659	12.317	2.22			
4	1	3013	11.4	2.54	2.60	0.11	4.27
	2	3230	11.417	2.73			
	3	3011	12.3333	2.53			

Table 7.16. Part I - Replicate 1, Run 4 Results: pH 7, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Phenol							
Control	1	2433	5.233	2.54	2.56	0.07	2.60
	2	2393	5.233	2.50			
	3	2524	5.233	2.63			
1	1	2455	5.25	2.57	2.54	0.10	3.85
	2	2315	5.233	2.43			
	3	2505	5.233	2.61			
2	1	2539	5.233	2.65	2.48	0.22	9.06
	2	2459	5.233	2.57			
	3	2112	5.233	2.23			
3	1	2063	5.233	2.18	2.25	0.07	3.16
	2	2153	5.233	2.27			
	3	2205	5.233	2.32			
4	1	2852	5.25	2.96	2.63	0.29	11.12
	2	2414	5.233	2.52			
	3	2290	5.233	2.40			
E1							
Control	1	3058	12.317	2.58	2.67	0.26	9.71
	2	2930	12.283	2.46			
	3	3490	12.283	2.96			
1	1	2651	12.317	2.22	2.11	0.12	5.88
	2	2378	12.3	1.98			
	3	2576	12.3	2.15			
2	1	2579	12.3	2.15	2.18	0.09	4.25
	2	2719	12.317	2.28			
	3	2514	12.3	2.10			
3	1	2619	12.317	2.19	2.16	0.05	2.29
	2	2527	12.3	2.11			
	3	2629	12.317	2.20			
4	1	3253	12.317	2.75	2.61	0.13	4.98
	2	3063	12.3	2.58			
	3	2963	12.283	2.49			

Table 7.17. Part I - Replicate 1, Run 4.2 Phenol Results: pH 7, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1726	7.717	1.84	1.92	0.30	15.54
	2	2216	7.667	2.33			
	3	1492	7.783	1.61			
	4	1792	8.017	1.91			
1	1	562	7.717	0.69	1.24	0.39	31.69
	2	1090	7.683	1.21			
	3	1361	7.7	1.48			
	4	1435	8	1.56			
2	1	1252	7.717	1.37	1.30	0.08	5.90
	2	1098	7.683	1.22			
	3	1193	7.683	1.32			
	4	1456	8.017	1.58			
3	1	1647	7.733	1.77	1.54	0.36	23.13
	2	1209	7.7	1.33			
	3	1783	7.683	1.90			
	4	1022	8.017	1.15			
4	[redacted]				1.79	0.13	7.27
	2	1783	7.7	1.90			
	3	1712	7.667	1.83			
	4	1528	8.033	1.65			

Results excluded from calculations [redacted]

Table 7.18. Part I - Replicate 1, Run 4.2 E1 Results: pH 7, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	2480	14.65	2.07	2.07	0.24	11.47
	2	2728	14.633	2.28			
	3	2109	14.783	1.74			
	4	2614	14.95	2.18			
1	1	1087	14.633	0.84	1.12	0.20	18.15
	2	1498	14.633	1.20			
	3	1427	14.633	1.14			
	4	1629	14.933	1.32			
2	1	1564	14.633	1.26	1.32	0.15	11.46
	2	1354	14.633	1.07			
	3	1695	14.633	1.37			
	4	1937	14.933	1.59			
3	1	1666	14.65	1.35	1.39	0.27	19.14
	2	1443	14.633	1.15			
	3	2146	14.633	1.77			
	4	1606	14.95	1.30			
4	[redacted]				1.82	0.04	2.15
	2	2146	14.633	1.77			
	3	2219	14.633	1.84			
	4	2226	14.933	1.84			

Results excluded from calculations [redacted]

Table 7.19. Part I - Replicate 1, Run 5 Results: pH 4, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Phenol							
Control	1	1998	6.8	2.11	2.50	0.42	16.65
	2	2328	6.833	2.44			
	3	2832	6.733	2.94			
1	1	1401	6.733	1.52	1.52	0.03	2.18
	2	1425	6.8	1.55			
	3	1359	6.833	1.48			
2	1	1555	6.833	1.67	1.70	0.03	1.74
	2	1577	6.817	1.70			
	3	1614	6.733	1.73			
3	1	1309	6.833	1.43	1.69	0.24	13.96
	2	1776	6.817	1.89			
	3	1623	6.733	1.74			
4	1	1961	6.833	2.08	2.03	0.05	2.32
	2	1866	6.733	1.98			
	3	1912	6.733	2.03			
E1							
Control	1	2186	14.267	1.81	2.50	0.87	34.62
	2	2661	14.283	2.23			
	3	4074	14.183	3.47			
1	1	396	14.233	0.23	0.21	0.10	47.17
	2	255	14.333	0.10			
	3	479	14.283	0.30			
2	1	404	14.36	0.24	0.49	0.24	49.43
	2	722	14.267	0.52			
	3	951	14.167	0.72			
3	1	1190	14.35	0.93	1.01	0.23	22.56
	2	1075	14.267	0.83			
	3	1567	14.167	1.26			
4	1	1646	14.283	1.33	1.75	0.36	20.78
	2	2400	14.15	2.00			
	3	2310	14.167	1.92			

Table 7.20. Part I - Replicate 1, Run 6 Results: pH 8.5, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Phenol							
Control	1	2184	6.717	2.30	2.15	0.14	6.34
	2	2027	6.717	2.14			
	3	1909	6.717	2.02			
1	1	954	6.733	1.08	0.93	0.13	14.04
	2	711	6.717	0.84			
	3	744	6.7	0.87			
2	1	1068	6.717	1.19	1.17	0.04	3.32
	2	997	6.717	1.12			
	3	1061	6.717	1.19			
3	1	1489	6.733	1.61	1.58	0.07	4.51
	2	1377	6.717	1.50			
	3	1511	6.717	1.63			
4	1	1483	6.717	1.60	1.66	0.10	6.16
	2	1481	6.7	1.60			
	3	1661	6.7	1.78			
E1							
Control	1	4128	14.167	3.52	2.56	0.83	32.45
	2	2585	14.15	2.16			
	3	2417	14.15	2.01			
1	1	1092	14.167	0.84	0.84	0.04	5.09
	2	1138	14.167	0.88			
	3	1041	14.15	0.80			
2	1	1549	14.167	1.25	1.14	0.11	9.63
	2	1301	14.167	1.03			
	3	1450	14.15	1.16			
3	1	2364	14.167	1.96	1.82	0.13	7.11
	2	2078	14.15	1.71			
	3	2163	14.167	1.79			
4	1	2282	14.167	1.89	1.84	0.10	5.66
	2	2088	14.15	1.72			
	3	2302	14.15	1.91			

Table 7.21. Part I - Replicate 1, Run 7 Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Phenol							
Control	1	2281	6.55	2.39	2.37	0.08	3.46
	2	2332	6.567	2.44			
	3	2170	6.567	2.28			
1	1	921	6.5	1.05	1.74	0.63	36.05
	2	2154	6.55	2.27			
	3	1804	6.567	1.92			
2	1	2168	6.583	2.28	2.01	0.25	12.68
	2	1658	6.567	1.78			
	3	1854	6.567	1.97			
3	1	1879	6.583	1.99	1.93	0.20	10.27
	2	1584	6.567	1.70			
	3	1965	6.567	2.08			
4	1	1920	6.583	2.04	1.99	0.06	3.13
	2	1799	6.583	1.92			
	3	1889	6.567	2.00			
E1							
Control	1	3458	13.933	2.93	2.44	0.56	23.12
	2	2203	13.917	1.82			
	3	3037	13.9	2.56			
1	1	1748	13.883	1.42	1.56	0.12	8.03
	2	2027	13.933	1.67			
	3	1931	13.917	1.58			
2	1	2378	13.933	1.98	1.71	0.31	18.33
	2	1685	13.917	1.37			
	3	2174	13.917	1.80			
3	1	1852	13.933	1.51	1.60	0.10	6.39
	2	1917	13.933	1.57			
	3	2077	13.917	1.71			
4	1	2712	13.933	2.27	1.97	0.46	23.47
	2	1767	13.95	1.44			
	3	2633	13.9	2.20			

Table 7.22. Part I - Replicate 1, Run 7.2 Phenol Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1596	8.033	1.71	1.75	0.37	21.26
	2	1119	7.933	1.24			
	3	1960	8	2.08			
	4	1862	8	1.98			
1	1	1519	8.05	1.64	2.00	0.28	13.86
	2	1877	8.067	1.99			
	3	1941	8.017	2.06			
	4	2198	8	2.31			
2	1	1933	8.05	2.05	2.08	0.03	1.63
	2	1944	8.05	2.06			
	3	1957	8	2.07			
	4	2010	8	2.12			
3	1	1906	8.05	2.02	1.86	0.12	6.24
	2	1685	8.033	1.80			
	3	1638	8.017	1.76			
	4	1728	8	1.85			
4	1	1869	8.05	1.99	1.90	0.16	8.49
	2	1927	8.05	2.04			
	3	1556	8	1.68			
	4	1779	8	1.90			

Table 7.23. Part I - Replicate 1, Run 7.2 E1 Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	2111	14.95	1.74	1.92	0.32	16.46
	2	1925	14.9	1.58			
	3	2711	14.917	2.27			
	4	2500	14.9	2.08			
1	1	898	14.95	0.67	0.73	0.08	10.56
	2	881	14.95	0.66			
	3	1048	14.917	0.80			
	4	1032	14.9	0.79			
2	1	1314	14.95	1.04	0.95	0.12	12.82
	2	1263	14.95	0.99			
	3	1007	14.9	0.77			
	4	1254	14.9	0.99			
3	1	1447	14.95	1.16	1.13	0.08	7.07
	2	1473	14.95	1.18			
	3	1482	14.917	1.19			
	4	1288	14.917	1.02			
4	1	1825	14.95	1.49	1.59	0.14	8.92
	2	1966	14.95	1.61			
	3	1822	14.917	1.49			
	4	2164	14.9	1.79			

Table 7.24. Part I - Replicate 1, Run 7.3 Phenol Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1095	7.95	1.22	1.21	0.06	5.03
	2	1017	7.933	1.14			
	3	1080	7.75	1.20			
	4	1167	7.75	1.29			
1	1	1237	7.933	1.36	1.20	0.14	12.00
	2	1007	7.933	1.13			
	3	912	7.767	1.04			
	4	1154	7.75	1.28			
2	1	1290	7.933	1.41	1.35	0.15	11.14
	2	1028	7.933	1.15			
	3	1387	7.767	1.51			
	4	1212	7.75	1.33			
3	1	1263	7.933	1.39	1.28	0.17	12.92
	2	1025	7.933	1.15			
	3	1004	7.767	1.13			
	4	1335	7.733	1.46			
4	1	922	7.95	1.05	1.20	0.25	21.01
	2	796	7.933	0.92			
	3	1315	7.767	1.44			
	4	1262	7.733	1.38			

Table 7.25. Part I - Replicate 1, Run 7.3 E1 Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1902	14.867	1.56	1.48	0.12	8.25
	2	1687	14.867	1.37			
	3	1706	14.7	1.38			
	4	1962	14.7	1.61			
1	1	868	14.867	0.64	0.63	0.05	8.52
	2	853	14.867	0.63			
	3	769	14.7	0.56			
	4	915	14.7	0.69			
2	1	708	14.883	0.50	0.59	0.11	18.11
	2	695	14.883	0.49			
	3	940	14.7	0.71			
	4	868	14.683	0.64			
3	1	1271	14.867	1.00	0.92	0.10	10.68
	2	1150	14.867	0.89			
	3	1039	14.7	0.80			
	4	1272	14.267	1.00			
4	1	1778	14.867	1.45	1.26	0.13	10.55
	2	1454	14.867	1.16			
	3	1465	14.683	1.17			
	4	1551	14.683	1.25			

Table 7.26. Part I - Replicate 1, Run 7.4 Phenol Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1389	8.033	1.51	1.61	0.09	5.63
	2	1637	8.017	1.76			
	3	1545	8	1.66			
	4	1551	8	1.67			
1	1	1579	8.017	1.70	1.71	0.28	16.47
	2	1384	8.017	1.50			
	3	2001	8.017	2.12			
	4	1411	7.983	1.53			
2	1	1565	8.017	1.68	1.64	0.02	1.30
	2	1501	8	1.62			
	3	1544	8.017	1.66			
	4	1524	8.017	1.64			
3	1	1551	8	1.67	1.57	0.19	11.90
	2	1230	8.017	1.35			
	3	1655	8.017	1.77			
	4	1370	7.967	1.49			
4	1	1295	8.017	1.42	1.61	0.15	9.10
	2	1573	8.017	1.69			
	3	1630	8	1.75			
	4	1457	8	1.58			

Run identified as outlier by Q-test

Table 7.27 Part I - Replicate 1, Run 7.4 E1 Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	2876	14.967	2.42	2.50	0.13	5.34
	[redacted]						
	3	2894		2.43			
		3147	14.95	2.65			
1	1	1440	14.95	1.15	1.25	0.14	11.56
	2	1410	14.95	1.12			
	3	1767	14.95	1.44			
	4	1587	14.95	1.28			
2	[redacted]				1.51	0.04	2.75
	2	1799	14.933	1.47			
	3	1886	14.95	1.54			
	4	1874	14.95	1.53			
3	1	1926	14.95	1.58	1.76	0.36	20.36
	2	1722	14.95	1.40			
	3	2658	14.95	2.22			
	4	2219	14.95	1.84			
4	1	2264	14.95	1.88	2.19	0.23	10.68
	2	2680	14.95	2.24			
	3	2655	14.95	2.22			
	4	2904	14.93	2.44			

[redacted]

Table 7.28. Part I - Replicate 1, Run 7.5 Phenol Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1390	8.067	1.51	1.69	0.13	7.78
	2	1590	8.017	1.71			
	3	1707	8.067	1.82			
	4	1610	8.067	1.73			
1	1	1238	8.017	1.36	1.49	0.13	8.51
	2	1312	8.05	1.43			
	3	1538	8.05	1.66			
	4	1378	8.067	1.50			
2	1	1387	8.067	1.51	1.48	0.09	6.14
	2	1248	8.067	1.37			
	3	1345	8.067	1.47			
	4	1469	8.067	1.59			
3	1	1340	8.067	1.46	1.51	0.09	5.79
	2	1512	8.05	1.63			
	3	1313	8.067	1.43			
	4	1406	8.067	1.53			
4	1	1565	8.067	1.68	1.63	0.16	9.90
	2	1435	8.067	1.56			
	3	1323	8.067	1.44			
	4	1699	8.05	1.82			

Table 7.29. Part I - Replicate 1, Run 7.5 E1 Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	2745	14.967	2.30	2.95	0.46	15.43
	2	3591	14.967	3.05			
	3	3945	14.967	3.36			
	4	3661	14.983	3.11			
1	1	1478	14.95	1.18	1.36	0.14	10.27
	2	1649	14.967	1.33			
	3	1843	14.967	1.50			
	4	1767	14.967	1.44			
2	1	1656	14.967	1.34	1.66	0.24	14.43
	2	1986	14.967	1.63			
	3	2296	14.983	1.90			
	4	2123	14.967	1.75			
3	1	2457	14.967	2.05	2.01	0.10	4.82
	2	2257	14.967	1.87			
	3	2450	14.967	2.04			
	4	2506	14.967	2.09			
4	1	2746	14.967	2.30	2.49	0.24	9.71
	2	3136	14.983	2.64			
	3	2706	14.983	2.27			
	4	3250	14.967	2.75			

Table 7.30. Part 1 - Replicate 1, Run 8 Results: pH 4, $O_3/H_2O_2 = 4:1$

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Phenol							
Control	1	2204	6.817	2.32	2.67	0.62	23.14
	2	2194	6.8	2.31			
	3	3279	6.833	3.38			
1	1	1256	6.533	1.38	1.54	0.16	10.41
	2	1580	6.8	1.70			
	3	1423	6.8	1.54			
2	1	1540	6.533	1.66	1.53	0.22	14.66
	2	1541	6.783	1.66			
	3	1148	6.767	1.27			
3	1	2097	6.55	2.21	2.15	0.24	11.16
	2	1773	6.833	1.89			
	3	2248	6.833	2.36			
4	1	1845	6.7	1.96	2.01	0.34	16.73
	2	1581	6.8	1.70			
	3	2255	6.817	2.37			
E1							
Control	1	2633	14.267	2.20	2.96	1.18	39.89
	2	2819	14.267	2.37			
	3	5043	14.267	4.33			
1	1	413	13.883	0.24	0.19	0.05	25.88
	2	299	14.267	0.14			
	3	359	14.267	0.20			
2	1	1096	13.9	0.85	0.75	0.13	17.13
	2	819	14.267	0.60			
	3	1031	14.233	0.79			
3	1	2089	13.883	1.72	1.68	0.26	15.74
	2	1719	14.283	1.40			
	3	2312	14.267	1.92			
4	1	2444	14.217	2.03	2.34	0.42	18.10
	2	2587	14.283	2.16			
	3	3338	14.267	2.82			

Table 7.31. Part I - Replicate 1, Run 8.2 Phenol Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	2095	8.033	2.21	1.82	0.35	19.15
	2	1273	7.667	1.39			
	3	1859	7.667	1.98			
	4	1600	7.667	1.72			
1	1	964		1.09	1.38	0.17	12.18
	2	1443	8.033	1.56			
	3	1117	7.667	1.24			
	4	1212	7.667	1.33			
	5	1201	7.65	1.32			
2	1	1830	8.05	1.95	1.46	0.06	3.84
	[redacted]						
	3	1308	7.667	1.43			
	4	1302	7.65	1.42			
	5	1403	7.667	1.52			
3	1	2146	8.033	2.26	1.62	0.48	29.48
	2	1006	7.433	1.13			
	3	1312	7.667	1.43			
	4	1538	7.667	1.66			
4	1	2308	8.033	2.42	1.79	0.19	10.62
	2	1465	7.683	1.59			
	3	1710	7.667	1.83			
	4	1844	7.65	1.96			

Results excluded from calculation [redacted]

Table 7.32. Part I - Replicate 1, Run 8.2 E1 Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	2089	14.983	1.72	1.52	0.21	13.73
	2	1544	14.617	1.24			
	3	1819	14.617	1.48			
	4	1976	14.617	1.62			
1	2	158	14.983	0.02	0.03	0.01	30.41
	3	177	14.7	0.04			
		172	14.65	0.03			
	[redacted]						
	1			-0.12			
2	[redacted]				0.09	0.01	16.77
	3	255	14.633	0.10			
	4	221	14.633	0.07			
		238	14.617	0.09			
	1			-0.12			
3	1	1353	14.983	1.07	0.80	0.22	27.26
	2	830	14.533	0.61			
	3	857	14.617	0.64			
	4	1120	14.617	0.87			
4	1	1622	14.967	1.31	1.23	0.24	19.50
	2	1742	14.617	1.42			
	3	1225	14.617	0.96			
	4	1631	14.617	1.32			

Results excluded from calculation [redacted]

Table 7.33. Part I - Replicate 1, Run 9 Results: pH 8.5, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Phenol							
Control	1	2318	6.8	2.43	2.18	0.22	9.86
	2	1973	6.817	2.09			
	3	1916	6.8	2.03			
1	1	948	6.817	1.07	1.28	0.27	21.31
	2	1057	6.767	1.18			
	3	1471	6.8	1.59			
2	1	1419	6.817	1.54	1.54	0.10	6.19
	2	1318	6.817	1.44			
	3	1510	6.817	1.63			
3	1	1480	6.8	1.60	1.66	0.08	4.77
	2	1635	6.8	1.75			
	3	1522	6.8	1.64			
4	1	1760	6.817	1.88	1.91	0.18	9.42
	2	1626	6.8	1.74			
	3	1985	6.833	2.10			
E1							
Control	1	3584	14.267	3.04	2.78	0.25	9.03
	2	3015	14.283	2.54			
	3	3273	14.267	2.77			
1	1	1435	14.267	1.14	1.62	0.42	26.03
	2	2126	14.233	1.75			
	3	2351	14.283	1.95			
2	1	1578	14.267	1.27	1.77	0.43	24.46
	2	2369	14.267	1.97			
	3	2475	14.283	2.06			
3	1	2694	14.267	2.25	2.36	0.10	4.29
	2	2806	14.25	2.35			
	3	2923	14.267	2.46			
4	1	3371	14.283	2.85	2.62	0.24	9.21
	2	3143	14.267	2.65			
	3	2825	14.283	2.37			

Table 7.34. Part I - Replicate 2, Run 1 Phenol Results: pH 8.5, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	943	8.033	1.07	1.37	0.29	21.23
	2	1090	7.583	1.21			
	3	1357	7.633	1.48			
	4	1608	7.567	1.73			
1	1	280	8.033	0.41	0.35	0.05	15.46
	2	184	7.583	0.32			
	3	187	7.433	0.32			
	[redacted]						
2	1	184	8.033	0.32	0.43	0.08	18.37
	2	327	7.6	0.46			
	3	369	7.55	0.50			
	4	305	7.567	0.44			
3	1	622	8.05	0.75	0.95	0.15	16.18
	2	776	7.617	0.90			
	3	926	7.6	1.05			
	4	960	7.583	1.09			
4	1	818	8.033	0.94	1.14	0.23	20.19
	2	806	7.617	0.93			
	3	1181	7.6	1.30			
	4	1241	7.583	1.36			

[redacted], as determined by Q-test

Table 7.35. Part I - Replicate 2, Run 1 E1 Results: pH 8.5, $O_3/H_2O_2 = 4:1$

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1936	15	1.59	1.79	0.38	21.37
	2	2113	14.5	1.74			
	3	1820	14.533	1.48			
	4	2789	14.5	2.34			
1	1	382	15.017	0.22	0.21	0.01	3.89
	2	380	14.5	0.21			
	3	365	14.5	0.20			
	[redacted]						
2	1	839	15	0.62	0.73	0.15	20.61
	2	809	14.5	0.59			
	3	1067	14.517	0.82			
	4	1159	14.5	0.90			
3	1	1490	15.017	1.19	1.30	0.15	11.33
	2	1444	14.5	1.15			
	3	1777	14.517	1.45			
	4	1727	14.5	1.40			
4	1	1597	15	1.29	1.35	0.22	16.35
	2	1367	14.517	1.08			
	3	1750	14.5	1.42			
	4	1961	14.5	1.61			

[redacted], as determined by Q-test

Table 7.36. Part I - Replicate 2, Run 2 Phenol Results: pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1052	8.033	1.18	1.09	0.07	6.53
	2	904	8	1.03			
	3	911	8	1.04			
	4	1002	8.017	1.13			
1	1	510	7.9	0.64	0.50	0.10	19.70
	2	353	8.017	0.48			
	3	352	8	0.48			
		271	8	0.40			
2	1	482	7.867	0.61	0.58	0.05	8.16
	2	457	8.017	0.59			
	3	474	8	0.60			
	4	378	7.983	0.51			
3	1	596	8.067	0.72	0.68	0.09	13.02
	2	620	8.033	0.75			
	3	422	8	0.55			
	4	581	7.983	0.71			
4	1	897	8.033	1.02	0.89	0.09	10.33
	2	680	8	0.81			
	3	731	8	0.86			
	4	751	8.017	0.88			

Table 7.37. Part I - Replicate 2, Run 2 E1 Results: pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	2110	14.983	1.74	1.72	0.03	1.62
	2	2116	14.95	1.75			
	3	2046	14.95	1.68			
	4	2094	14.95	1.73			
1	1	624	14.133	0.43	0.51	0.07	12.71
	2	771	14.967	0.56			
	3	693	14.95	0.49			
	4	782	14.95	0.57			
2	1	714	14.85	0.51	0.65	0.13	19.85
	2	977	14.983	0.74			
	3	1024	14.95	0.78			
	4	795	14.933	0.58			
3	1	1137	15	0.88	0.86	0.11	13.28
	2	959	14.983	0.73			
	3	1091	14.95	0.84			
	4	1274	14.933	1.00			
4	1	1386	14.983	1.10	1.27	0.13	10.41
	2	1690	14.95	1.37			
	3	1699	14.95	1.38			
	4	1522	14.95	1.22			

Table 7.38. Part I - Replicate 2, Run 3 Phenol Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1173	7.933	1.30	1.13	0.23	20.12
	[redacted]						
	3	743	7.683	0.87			
	4	1097	7.667	1.22			
1	1	823	7.9	0.95	0.98	0.13	12.94
	2	743	7.883	0.87			
	3	822	7.883	0.95			
	4	1042	7.683	1.17			
2	1	840	7.867	0.97	1.09	0.17	15.87
	[redacted]						
	3	897	7.7	1.02			
	4	1168	7.683	1.29			
3	1	881	7.917	1.01	0.97	0.05	4.91
	2	795	7.9	0.92			
	3	895	7.667	1.02			
	4	818	7.683	0.94			
4	1	854	7.917	0.98	0.99	0.01	0.81
	2	870	7.9	1.00			
	3	864	7.667	0.99			
	[redacted]						

[redacted]

Table 7.39. Part I - Replicate 2, Run 3 E1 Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1966	14.867	1.61	1.64	0.02	1.37
	[redacted]						
	3	2002	14.533	1.64			
	4	2015	14.533	1.66			
1	1	752	14.85	0.54	0.43	0.16	36.48
	2	605	14.85	0.41			
	3	761	14.85	0.55			
	4	380	14.533	0.21			
2	1	834	14.85	0.61	0.63	0.01	2.18
	[redacted]						
	3	860	14.533	0.64			
	4	862	14.533	0.64			
3	1	1215	14.85	0.95	1.01	0.09	9.02
	2	1334	14.833	1.06			
	3	1409	14.517	1.12			
	4	1187	14.533	0.93			
4	1	1649	14.85	1.33	1.47	0.12	8.02
	2	1867	14.85	1.53			
	3	1892	14.517	1.55			
	[redacted]						

[redacted]

Table 7.40. Part I - Replicate 2, Run 3.2 Phenol Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	728	7.767	0.86	0.91	0.05	5.85
	2	835	7.8	0.96			
	3	777	7.783	0.90			
1	1	484	7.717	0.61	0.60	0.05	7.50
	2	439	7.783	0.57			
	3	429	7.733	0.56			
	4	528	7.783	0.66			
2	1	449	7.8	0.58	0.64	0.07	10.39
	2	481	7.783	0.61			
	3	605	7.783	0.73			
	4	511	7.783	0.64			
3	1	617	7.817	0.75	0.75	0.09	12.19
	2	744	7.783	0.87			
	3	616	7.8	0.74			
	4	518	7.783	0.65			
4	1	727	7.783	0.85	0.91	0.08	9.01
	2	905	7.8	1.03			
	3	732	7.767	0.86			
	4	776	7.767	0.90			

Table 7.41. Part I - Replicate 2, Run 3.2 E1 Results: pH 4, O_3/H_2O_2 =.1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1947	14.717	1.60	1.60	0.03	1.65
	2	1931	14.733	1.58			
	3	1989	14.733	1.63			
1	1	588	14.733	0.40	0.43	0.04	9.89
	2	675	14.733	0.47			
	3	578	14.717	0.39			
	4	655	14.717	0.46			
2	1	688	14.733	0.49	0.63	0.13	20.86
	2	1014	14.717	0.77			
	3	922	14.733	0.69			
	4	763	14.717	0.55			
3	1	959	14.733	0.73	0.92	0.17	18.29
	2	1411	14.717	1.12			
	3	1119	14.733	0.87			
	4	1244	14.733	0.98			
4	1	1195	14.733	0.93	1.22	0.21	16.81
	2	1650	14.733	1.33			
	3	1535	14.733	1.23			
	4	1722	14.733	1.40			

Table 7.42. Part I - Replicate 2, Run 4 Phenol Results: pH 4, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1768	7.733	1.89	1.93	0.07	3.51
	2	1865	7.733	1.98			
1	1	1539	7.75	1.66	1.34	0.26	19.78
	2	1326	7.733	1.45			
	3	1049	7.733	1.17			
	4	951	7.717	1.08			
2	1	1659	7.733	1.78	1.49	0.20	13.60
	2	1244	7.733	1.37			
	3	1383	7.733	1.50			
	4	1206	7.733	1.33			
3	[redacted]				1.88	0.08	4.12
	2	1692	7.733	1.81			
	3	1758	7.717	1.88			
	4	1848		1.96			
4	1	1526	7.717	1.65	1.86	0.20	10.66
	2	1781	7.717	1.90			
	3	1921	7.717	2.04			
	4	1605		1.72			

Sample 1 discarded from analysis - indications that E1 wasn't present at all in sample. peak was very iffy - looked like background methanol hump

[redacted] – phenol and E1

Table 7.43. Part I - Replicate 2, Run 4 E1 Results: pH 4, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	2625	14.667	2.19	2.27	0.11	4.94
	2	2805	14.667	2.35			
1	1	1162	14.7	0.90	1.30	0.43	33.11
	2	2270	14.917	1.88			
	3	1337	15.017	1.06			
	4	1676	14.983	1.36			
2	1	519	14.683	0.34	0.28	0.06	20.05
	2	467	14.683	0.29			
	3	444	14.667	0.27			
	4	368	14.683	0.20			
3	[redacted]				1.26	0.10	7.54
	2	1681	14.683	1.36			
	3	1557	14.667	1.25			
	4	1466		1.17			
4	1	1894	14.667	1.55	1.70	0.14	7.96
	2	2196	14.683	1.82			
	3	2089	14.667	1.72			
	4	1779		1.45			

Sample 1 discarded from analysis - indications that E1 wasn't present at all in sample. peak was very iffy - looked like background methanol hump

[redacted] – phenol and E1

Table 7.44. Part I - Replicate 2, Run 5 Phenol Results: pH 4, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	2240	7.767	2.35	2.69	0.33	12.38
	2	2758	7.767	2.87			
	3	2370	7.733	2.48			
	4	2966	7.75	3.07			
1	1	3009	7.767	3.11	2.11	0.29	13.87
	2	1985	7.75	2.10			
	3	2296	7.733	2.41			
	4	1705	7.733	1.82			
2	[redacted]				2.28	0.02	0.89
	2	2168	7.733	2.28			
	3	2151	7.767	2.26			
	4	2192	7.75	2.30			
3	1	2248	7.75	2.36	2.32	0.06	2.47
	2	2166	7.75	2.28			
4	1	2415	7.767	2.53	2.52	0.22	8.64
	2	2128	7.767	2.24			
	3	2665	7.767	2.77			
	4	2428	7.75	2.54			

[redacted] 1 – HPLC replicate 2- denoted by Q-test

Table 7.45. Part I - Replicate 2, Run 5 E1 Results: pH 4, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	2385	14.35	1.98	2.56	0.41	16.09
	2	3494	14.717	2.96			
	3	3129	14.7	2.64			
	4	3146	14.7	2.65			
1	1	[redacted]			0.19	0.02	12.99
	2	347	14.683	0.19			
	3	322	14.7	0.16			
	4	377	14.683	0.21			
2	[redacted]				0.63	0.04	6.47
	2	888	14.683	0.66			
	3	798	14.7	0.58			
	4	860	14.7	0.64			
3	1	1528	14.7	1.23	1.22	0.00	0.25
	2	1523	14.7	1.22			
4	1	2268	14.7	1.88	1.74	0.12	6.88
	2	1939	14.7	1.59			
	3	2143	14.7	1.77			
	4	2098	14.7	1.73			

[redacted] 1 – denoted by Q-test 2 –HPLC replicate

Table 7.46. Part I - Replicate 2, Run 6 Phenol Results: pH 8.5, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1949	7.967	2.06	1.90	0.15	7.98
	2	1705	7.983	1.82			
	3	1609	7.967	1.73			
	4	1863	7.95	1.98			
1	1	1015	7.967	1.14	1.17	0.03	2.87
	2	1087	8	1.21			
	3	1070	7.983	1.19			
	4	1028	7.95	1.15			
2	1	1191	7.967	1.31	1.41	0.16	11.45
	2	1357	7.983	1.48			
	3	1489	7.967	1.61			
	4	1128	7.95	1.25			
3	1	1238	8.017	1.36	1.39	0.15	10.55
	2	1187	7.967	1.31			
	3	1150	8	1.27			
	4	1478	7.967	1.60			
4	1	1188	7.967	1.31	1.58	0.22	13.59
	2	1506	7.983	1.63			
	3	1715	7.967	1.83			
	4	1440	7.967	1.56			

Table 7.47. Part I - Replicate 2, Run 6 E1 Results: pH 8.5, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	3188	14.883	2.69	2.81	0.08	2.93
	2	3362	14.9	2.84			
	3	3371	14.9	2.85			
	4	3388	14.883	2.87			
1	1	1850	14.9	1.51	1.75	0.19	10.73
	2	2241	14.9	1.86			
	3	2328	14.9	1.93			
	4	2051	14.883	1.69			
2	1	2696	14.9	2.26	2.23	0.17	7.77
	2	2537	14.9	2.12			
	3	2922	14.9	2.46			
	4	2486	14.883	2.07			
3	1	2339	14.917	1.94	2.02	0.30	14.65
	2	2368	14.9	1.97			
	3	2094	14.917	1.73			
	4	2890	14.9	2.43			
4	1	2770	14.9	2.32	2.41	0.11	4.68
	2	2984	14.9	2.51			
	3	2973	14.9	2.50			
	4	2746	14.883	2.30			

Table 7.48. Part I - Replicate 2, Run 7 Phenol Results: pH 7, $O_3/H_2O_2 = 4:1$

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1597	7.817	1.72	1.66	0.07	4.50
	2	1490	7.8	1.61			
1	1	701	7.817	0.83	0.72	0.14	19.49
	2	393	7.75	0.52			
	3	596	7.783	0.72			
	4	689	7.8	0.82			
2	1	1217	7.817	1.34	1.25	0.14	11.27
	2	976	7.8	1.10			
	3	1048	7.8	1.17			
	4	1282	7.8	1.40			
3	1	1251	7.817	1.37	1.34	0.18	13.27
	2	1151	7.8	1.27			
	3	1445	7.783	1.57			
	4	1019	7.783	1.14			
4	1	1249	7.8	1.37	1.42	0.23	16.03
	2	1075	7.8	1.20			
	3	1247	7.767	1.37			
	4	1620	7.783	1.74			

Table 7.49. Part I - Replicate 2, Run 7 E1 Results: pH 7, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	3338	14.75	2.82	2.76	0.09	3.23
	2	3195	14.733	2.70			
1	1	1206	14.75	0.94	0.94	0.05	5.29
	2	1133	14.717	0.88			
	3	1270	14.717	1.00			
	4	1192	14.733	0.93			
2	1	2012	14.75	1.65	1.70	0.10	5.65
	2	1958	14.733	1.61			
	3	2211	14.733	1.83			
	4	2066	14.733	1.70			
3	1	1975	14.75	1.62	1.56	0.23	15.00
	2	1697	14.733	1.38			
	3	2261	14.717	1.87			
	4	1711	14.717	1.39			
4	1	2173	14.733	1.80	1.92	0.24	12.30
	2	2065	14.733	1.70			
	3	2329	14.717	1.93			
	4	2678	14.733	2.24			

Table 7.50. Part I - Replicate 2, Run 8 Phenol Results: pH 7, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1151	8.067	1.27	1.75	0.40	22.77
	2	1442	8.067	1.56			
	3	1991	8.083	2.11			
	4	1928	8.1	2.04			
1	1	1105	8.117	1.23	1.21	0.03	2.43
	2	1063	8.083	1.19			
2	1	943	8.1	1.07	1.35	0.27	20.18
	2	1582	8.083	1.70			
	3	1096	8.067	1.22			
	4	1273	8.067	1.39			
3	1	1118	8.083	1.24	1.42	0.17	11.79
	2	1215	8.083	1.34			
	3	1332	8.083	1.45			
	4	1510	8.083	1.63			
4	1	1330	8.083	1.45	1.43	0.07	5.03
	2	1220	8.083	1.34			
	3	1303	8.083	1.42			
	4	1396	8.083	1.52			

Table 7.51. Part I - Replicate 2, Run 8 E1 Results: pH 7, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	3004	15.017	2.53	2.89	0.43	14.87
	2	3065	15	2.58			
	3	4052	15.017	3.45			
	4	3543	15.017	3.00			
1	1	2338	15.033	1.94	1.88	0.08	4.20
	2	2211	15.017	1.83			
2	1	2190	15.033	1.81	2.07	0.24	11.41
	2	2765	15.017	2.32			
	3	2326	15	1.93			
	4	2640	15	2.21			
3	1	2408	15.017	2.00	2.16	0.11	5.22
	2	2601	15.017	2.17			
	3	2645	15.017	2.21			
	4	2704	15.017	2.26			
4	1	2577	15.017	2.15	2.32	0.16	6.95
	2	2682	15.017	2.24			
	3	3000	15.017	2.52			
	4	2821	15.017	2.37			

Table 7.52. Part I - Replicate 2, Run 9 Phenol Results: pH 8.5, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1544	8.033	1.66	1.71	0.11	6.64
	2	1742	8.033	1.86			
	3	1607	8.017	1.73			
	4	1472	8.017	1.59			
1	1	734	8.05	0.86	0.84	0.03	3.41
	2	693	8.05	0.82			
2	1	870	8.05	1.00	1.16	0.14	11.67
	2	1012	8.033	1.14			
	3	1055	8.017	1.18			
	4	1202	8.017	1.32			
3	1	1114	8.033	1.24	1.22	0.03	2.18
	2	1076	8.05	1.20			
4	1	1319	8.05	1.44	1.44	0.02	1.52
	2	1302	8.017	1.42			
	[redacted]						
	4	1346	8.017	1.47			

[redacted]

Table 7.53. Part I - Replicate 2, Run 9 E1 Results: pH 8.5, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	3270	14.983	2.76	2.90	0.13	4.43
	2	3624	14.967	3.07			
	3	3403	14.95	2.88			
	4	3425	14.967	2.90			
1	1	1604	14.983	1.29	1.27	0.04	3.00
	2	1543	14.983	1.24			
2	1	1871	14.983	1.53	1.72	0.16	9.44
	2	2114	14.983	1.74			
	3	2044	14.967	1.68			
	4	2316	14.967	1.92			
3	1	2176	14.967	1.80	1.82	0.03	1.85
	2	2230	14.983	1.85			
4	1	2416	14.967	2.01	2.19	0.15	6.96
	2	2720	14.967	2.28			
	[redacted]						
	4	2709	14.967	2.27			

[redacted]

Table 7.54. Part I - Control Run Results: No phenol, pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	3116	14.883	2.63	2.89	0.19	6.61
	2	3612	14.883	3.06			
	3	3525	14.883	2.99			
	4	3395	14.867	2.87			
1	1	654	14.883	0.46	0.45	0.01	2.22
	2	638	14.883	0.44			
2	1	1001	14.914	0.76	0.99	0.20	19.70
	2	1175	14.9	0.92			
	3	1375	14.883	1.09			
	4	1506	14.867	1.21			
3	1	1756	14.883	1.43	1.45	0.03	2.11
	2	1805	14.883	1.47			
4	1	2409	14.883	2.00	2.09	0.09	4.35
	2	2615	14.883	2.19			
	3	2500	14.867	2.08			

Table 7.55. Part I - Control Run Phenol Results: No TBA, pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1385	7.8	1.51	1.85	0.23	12.68
	2	1919	7.8	2.03			
	3	1778	7.783	1.89			
	4	1834	7.767	1.95			
1	1	875	7.817	1.00	1.09	0.07	6.82
	2	970	7.817	1.10			
	3	1057	7.783	1.18			
	4	948	7.8	1.07			
2	1	854	7.817	0.98	1.17	0.15	12.51
	2	1018	7.783	1.14			
	3	1160	7.783	1.28			
	4	1171	7.783	1.29			
3	1	1335	7.817	1.46	1.36	0.11	7.78
	2	1139	7.8	1.26			
	3	1320	7.8	1.44			
	4	1147	7.8	1.27			
4	1	1491	7.817	1.61	1.42	0.15	10.65
	2	1155	7.8	1.28			
	3	1356	7.783	1.48			
	4	1202	7.783	1.32			

Results excluded from calculation – applied ozone dose was too high

Table 7.56. Part I - Control Run E1 Results: No TBA, pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	2801	14.767	2.35	2.63	0.22	8.50
	2	3233	14.767	2.73			
	3	3041	14.75	2.56			
	4	3388	14.733	2.87			
1	1	1851	14.767	1.51	1.56	0.15	9.77
	2	1742	14.767	1.42			
	3	2151	14.75	1.78			
	4	1893	14.767	1.55			
2	1	1764	14.767	1.43	1.71	0.20	11.65
	2	2051	14.75	1.69			
	3	2241	14.75	1.86			
	4	2243	14.75	1.86			
3	1	2289	14.783	1.90	2.02	0.16	7.85
	2	2253	14.767	1.87			
	3	2554	14.767	2.13			
	4	2604	14.75	2.18			
4	1	2265	14.767	1.88	2.03	0.20	9.95
	2	2303	14.767	1.91			
	3	2769	14.75	2.32			
	4	2426	14.75	2.02			

Results excluded from calculation – applied ozone dose was too high

Appendix C: Rate constant sample calculations and results, Part I (direct O_3 experiments)

Relationship used to obtain $k_{O3\text{-}phenol}$ at given pH:

$$k_{appPhenol} = k_{O3/Phenol}\frac{10^{-pH}}{10^{-pKa}+10^{-pH}} + k_{O_3/Phenolate}\frac{10^{-pKa}}{10^{-pKa}+10^{-pH}}$$

(Deborde et al., 2005).

$kO3$,phenol = 1.30E+03 $M^{-1}s^{-1}$
$kO3$,phenolate = 1.40E+09 $M^{-1}s^{-1}$
pKa = 9.9

(Hoigné and Bader, 1983b)

Therefore:

pH 4 $k_{apparent\ phenol}$ = 3.06E+03 $M^{-1}s^{-1}$
pH 7 $k_{apparent\ phenol}$ = 1.76E+06 $M^{-1}s^{-1}$
pH 8.5 $k_{apparent\ phenol}$ = 5.36E+07 $M^{-1}s^{-1}$

$$\ln\left(\frac{[M(n)]}{[M(0)]}\right) = \ln\left(\frac{[R(n)]}{[R(0)]}\right) z_{rel}\frac{k_{oxidant}(M)}{k_{oxidant}(R)}$$ (Huber et al., 2003)

y = mx

$$m = z_{rel}\frac{k_{oxidant}(M)}{k_{oxidant}(R)} \rightarrow k_{oxidant}(M) = \frac{m\,k_{oxidant}(R)}{z_{rel}}$$

$$z_{rel} = \frac{O_3 : E1}{O_3 : Phenol}$$

E1: $C_{18}H_{22}O_2$
Phenol: C_6H_6O

$15O_3 + C_{18}H_{22}O_2 \rightarrow 18CO_2 + 11H_2O$ $\therefore$ O_3:E1 = 15

$4.67O_3 + C_6H_6O \rightarrow 6CO_2 + 3H_2O$ $\therefore$ O_3:Phenol = 4.67

z_{rel} = 3.212

Table 7.57. Part I - Replicate 1, Run 1 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 2:1

	Phenol (R) Concentration (µM)		E1 (M) Concentration (µM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	3.07	0.06	3.52	0.13
1	2.68	0.74	2.34	0.68
2	2.56	0.20	2.01	0.26
3	2.48	0.14	2.28	0.26
4	2.83	0.26	3.01	0.27
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.87	-0.13	0.67	-0.41
2	0.84	-0.18	0.57	-0.56
3	0.81	-0.21	0.65	-0.43
4	0.92	-0.08	0.86	-0.15

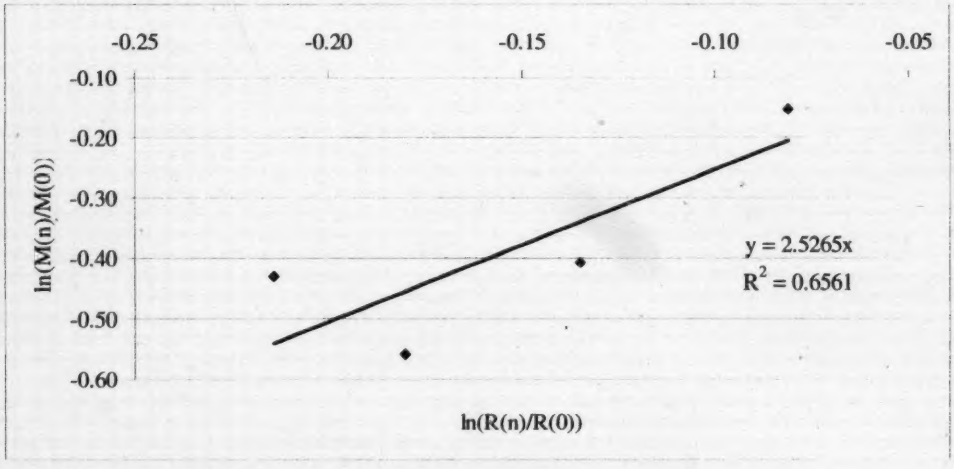

Figure 7.3. Competitive Kinetics Results, Replicate 1, Run 1: pH 7, O_3/H_2O_2 = 2:1

m = 2.5265
pH = 7

Therefore, $k_{O3\text{-phenol}}$ @ pH 7 = 1.76×10^6 $M^{-1}s^{-1}$

$$k_{O3-E1} = \frac{m \times k_{O3-phenol}}{z_{rel}}$$

$= (2.5265 \times 1.76 \times 10^6\ M^{-1}s^{-1})/3.212$

$= 1.39 \times 10^6\ M^{-1}s^{-1}$

Table 7.58. Part I - Replicate 1, Run 1.2 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 2:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.54	0.26	1.71	0.27
1	1.06	0.17	0.65	0.15
2	1.01	0.11	0.82	0.05
3	1.22	0.24	0.93	0.02
4	1.30	0.18	1.16	0.16
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.69	-0.37	0.38	-0.97
2	0.66	-0.42	0.48	-0.73
3	0.79	-0.23	0.54	-0.61
4	0.84	-0.17	0.68	-0.39

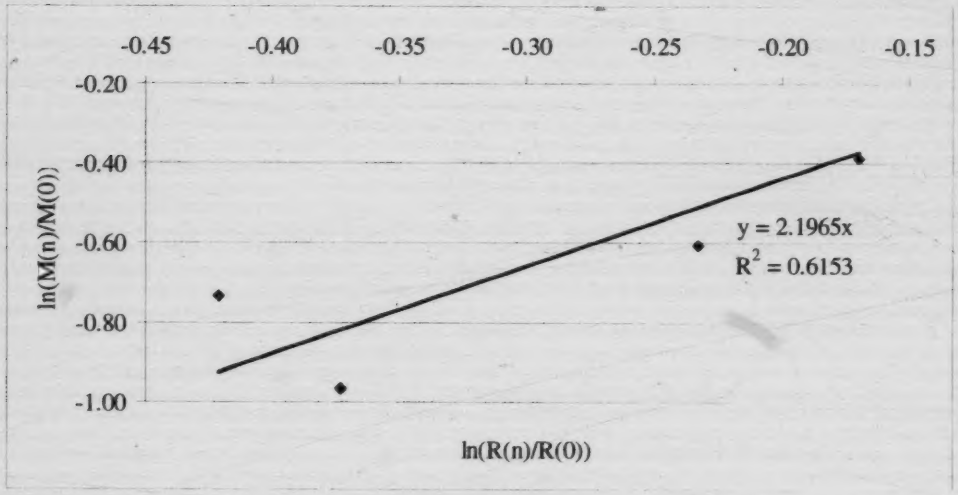

Figure 7.4. Competitive Kinetics Results, Replicate 1, Run 1.2: pH 7, O_3/H_2O_2 = 2:1

m = 2.1965
$k_{O3\text{-}E1} = 1.20 \times 10^6\ M^{-1}s^{-1}$

Table 7.59. Part I - Replicate 1, Run 1.3 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 2:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.44	0.24	1.97	0.05
1	0.74	0.24	0.67	0.14
2	1.19	0.23	0.82	0.16
3	1.60	0.29	1.24	0.19
4	1.13	0.11	1.32	0.04
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.52	-0.66	0.34	-1.08
2	0.82	-0.19	0.42	-0.88
3	1.11	0.10	0.63	-0.47
4	0.78	-0.24	0.67	-0.40

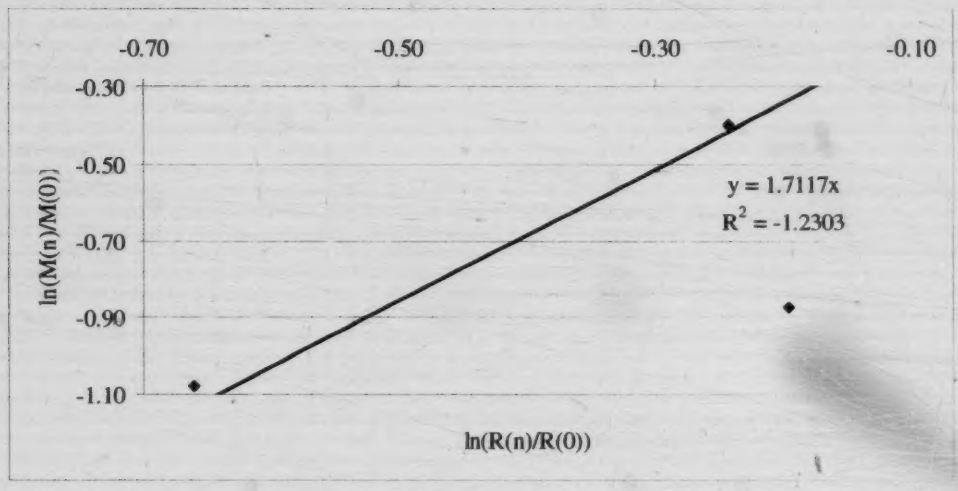

Figure 7.5. Competitive Kinetics Results, Replicate 1, Run 1.3: pH 7, O_3/H_2O_2 = 2:1

m = 1.7117
$k_{O3\text{-}E1} = 9.39 \times 10^5\ M^{-1}s^{-1}$

Table 7.60. Part I - Replicate 1, Run 1.4 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 2:1

	Phenol Concentration (µM)		E1 Concentration (µM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.64	0.06	2.82	0.07
1	1.13	0.07	1.35	0.09
2	1.31	0.14	1.71	0.16
3	1.35	0.19	1.92	0.14
4	1.59	0.12	2.17	0.22
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.69	-0.37	0.48	-0.74
2	0.80	-0.22	0.61	-0.50
3	0.82	-0.19	0.68	-0.38
4	0.97	-0.03	0.77	-0.26

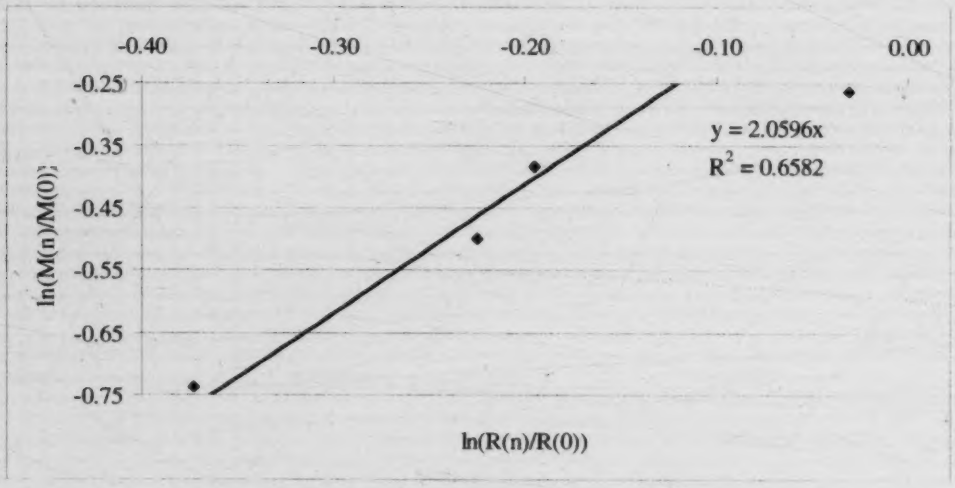

Figure 7.6. Competitive Kinetics Results, Replicate 1, Run 1.4: pH 7, O_3/H_2O_2 = 2:1

m = 2.0596
$k_{O3\text{-}E1} = 1.13 \times 10^6\ M^{-1}s^{-1}$

Table 7.61. Part I - Replicate 1, Run 2 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 2:1

	Phenol (R) Concentration (μM)		E1 (M) Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.54	0.02	3.07	0.17
1	2.39	0.20	1.98	0.18
2	2.64	0.22	2.56	0.31
3	3.01	0.43	2.54	0.18
4	2.56	0.12	2.89	0.29
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.94	-0.06	0.64	-0.44
2	1.04	0.04	0.83	-0.18
3	1.19	0.17	0.83	-0.19
4	1.01	0.01	0.94	-0.06

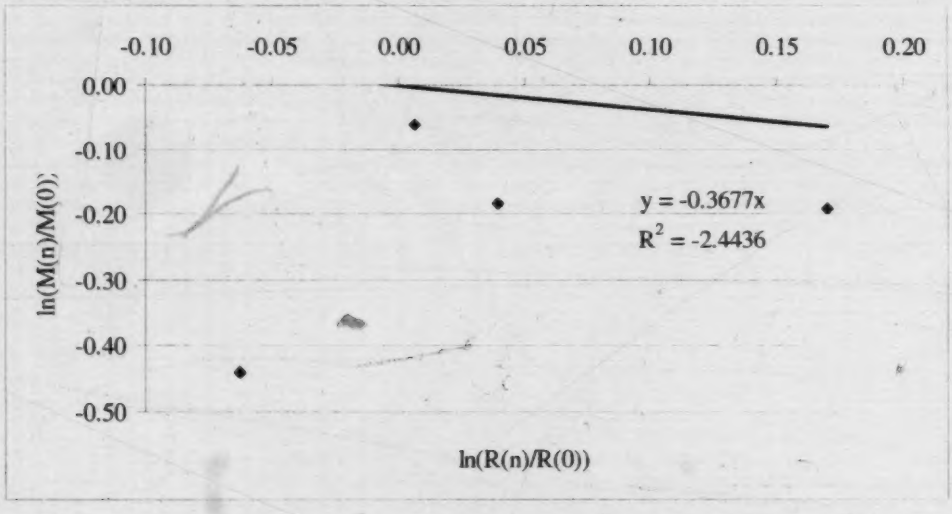

Figure 7.7. Competitive Kinetics Results, Replicate 1, Run 2: pH 8.5, O_3/H_2O_2 = 2:1

m = -0.3677
$k_{O3\text{-}E1} = -6.14 \times 10^6\ M^{-1}s^{-1}$

Table 7.62. Part I - Replicate 1, Run 2.2 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 2:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.67	0.15	1.93	0.08
1	0.77	0.09	0.63	0.18
2	1.07	0.05	1.02	0.01
3	1.26	0.26	1.03	0.25
4	1.40	0.03	1.39	0.03
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.46	-0.77	0.32	-1.13
2	0.64	-0.45	0.53	-0.64
3	0.75	-0.28	0.53	-0.63
4	0.84	-0.18	0.72	-0.32

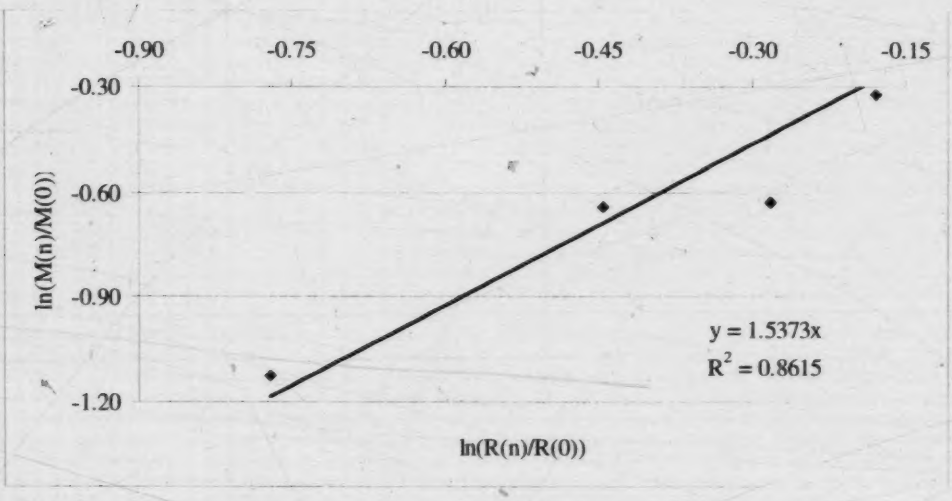

Figure 7.8. Competitive Kinetics Results, Replicate 1, Run 2.2: pH 8.5, O_3/H_2O_2 = 2:1

m = 1.5373
$k_{O3\text{-}E1} = 2.57 \times 10^7\ M^{-1}s^{-1}$

Table 7.63. Part I - Replicate 1, Run 3 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 4:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.40	0.01	2.57	0.17
1	1.71	0.42	1.00	0.18
2	2.29	0.09	1.62	0.11
3	2.20	0.12	2.16	0.14
4	2.72	0.12	2.54	0.00
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.71	-0.34	0.39	-0.95
2	0.96	-0.04	0.63	-0.46
3	0.92	-0.09	0.84	-0.17
4	1.13	0.13	0.99	-0.01

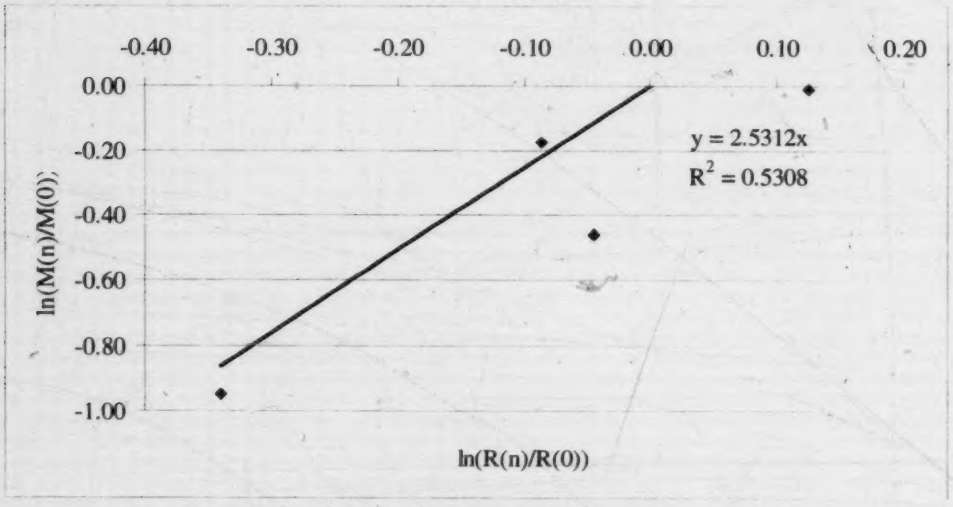

Figure 7.9. Competitive Kinetics Results, Replicate 1, Run 3: pH 7, O_3/H_2O_2 = 4:1

m = 2.5312
$k_{O3\text{-}E1} = 1.39 \times 10^6\ M^{-1}s^{-1}$

Table 7.64. Part I - Replicate 1, Run 4 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 1:2

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.56	0.07	2.67	0.26
1	2.54	0.10	2.11	0.12
2	2.48	0.22	2.18	0.09
3	2.25	0.07	2.16	0.05
4	2.63	0.29	2.61	0.13
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.99	-0.01	0.79	-0.23
2	0.97	-0.03	0.82	-0.20
3	0.88	-0.13	0.81	-0.21
4	1.03	0.03	0.04	-3.20

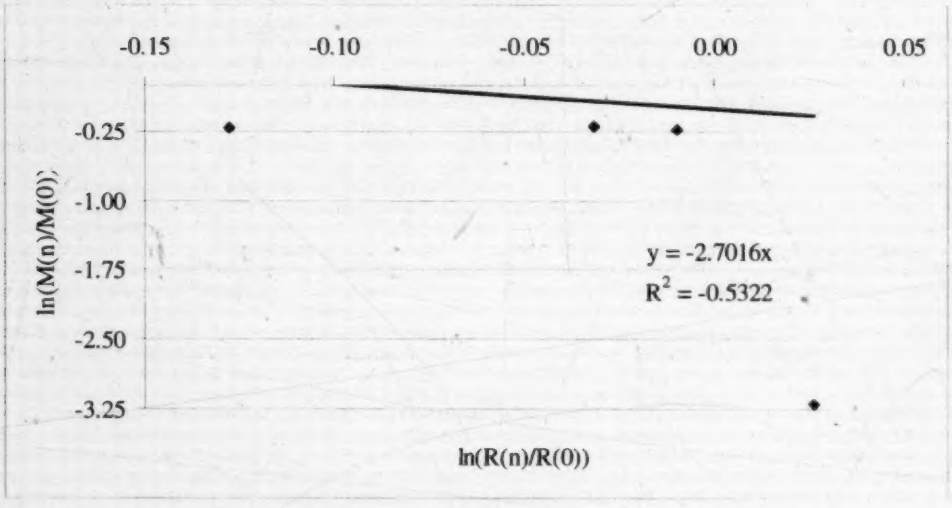

Figure 7.10. Competitive Kinetics Results, Replicate 1, Run 4: pH 7, O_3/H_2O_2 = 1:2

m = -2.7016
$k_{O3\text{-}E1} = -1.48 \times 10^6\ M^{-1}s^{-1}$

Table 7.65. Part 1 - Replicate 1, Run 4.2 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 1:2

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.92	0.30	2.07	0.24
1	1.24	0.39	1.12	0.20
2	1.30	0.08	1.24	0.15
3	1.54	0.36	1.39	0.27
4	1.79	0.13	1.82	0.04
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.64	-0.44	0.54	-0.61
2	0.68	-0.39	0.60	-0.51
3	0.80	-0.22	0.67	-0.40
4	0.93	-0.07	0.88	-0.13

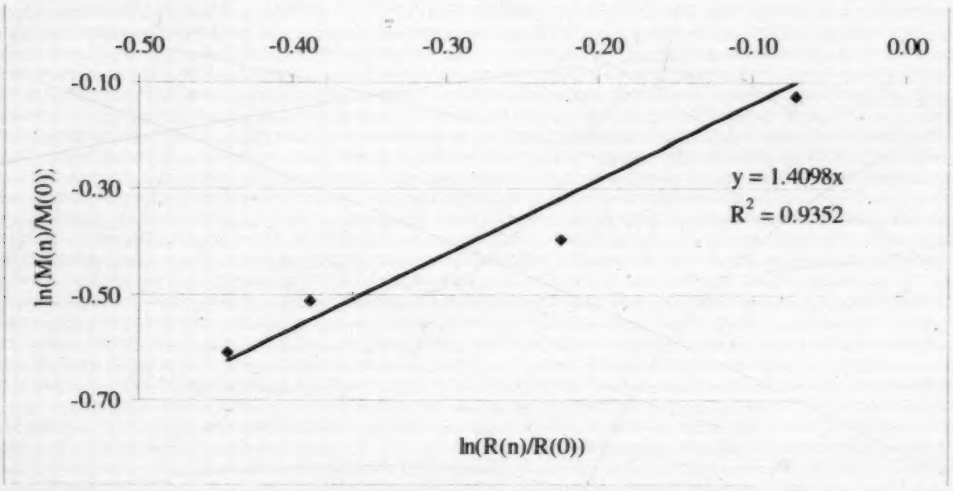

Figure 7.11. Competitive Kinetics Results, Replicate 1, Run 4.2: pH 7, O_3/H_2O_2 = 1:2

m = 1.4098
$k_{O3\text{-}E1} = 7.73 \times 10^5\ M^{-1}s^{-1}$

Table 7.66. Part I - Replicate 1, Run 5 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 2:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.50	0.42	2.50	0.87
1	1.52	0.03	0.21	0.10
2	1.70	0.03	0.49	0.24
3	1.69	0.24	1.01	0.23
4	2.03	0.05	1.75	0.36
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.61	-0.50	0.08	-2.47
2	0.68	-0.38	0.20	-1.63
3	0.68	-0.39	0.40	-0.91
4	0.81	-0.21	0.70	-0.36

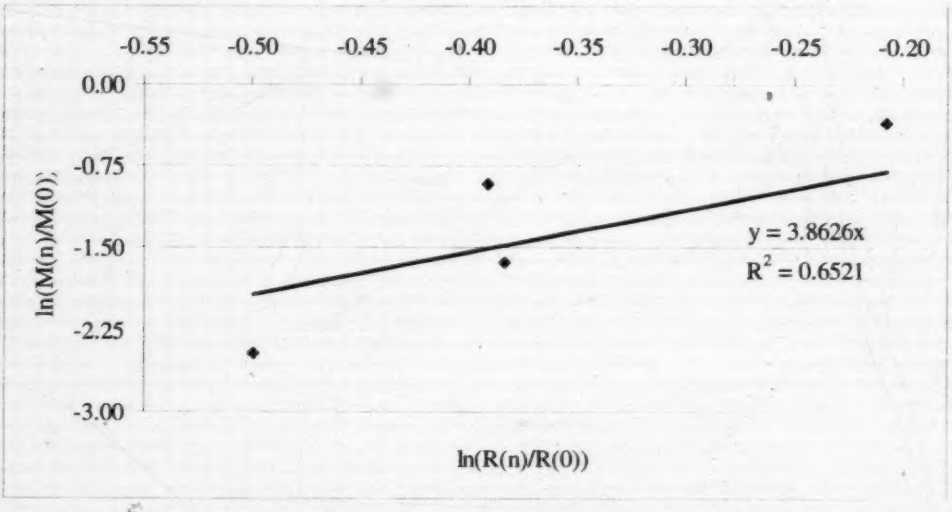

Figure 7.12. Competitive Kinetics Results, Replicate 1, Run 5: pH 4, O_3/H_2O_2 = 2:1

m = 3.8626
$k_{O3\text{-}E1} = 3.68 \times 10^3\ M^{-1}s^{-1}$

Table 7.67. Part I - Replicate 1, Run 6 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 4:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.15	0.14	2.56	0.83
1	0.93	0.13	0.84	0.04
2	1.17	0.04	1.14	0.11
3	1.58	0.07	1.82	0.13
4	1.60	0.00	1.81	0.12
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.43	-0.84	0.33	-1.11
2	0.54	-0.61	0.45	-0.81
3	0.73	-0.31	0.71	-0.34
4	0.74	-0.30	0.71	-0.35

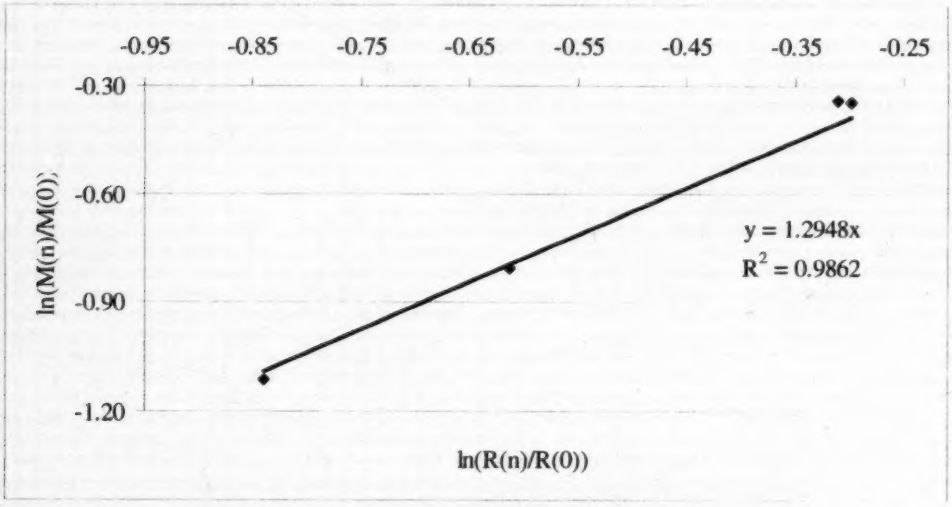

Figure 7.13. Competitive Kinetics Results, Replicate 1, Run 6: pH 8.5, O_3/H_2O_2 = 4:1

m = 1.2948
$k_{O3\text{-}E1} = 2.16 \times 10^7\ M^{-1}s^{-1}$

Table 7.68. Part I - Replicate 1, Run 7 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 1:2

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.37	0.08	2.44	0.56
1	1.74	0.63	1.56	0.12
2	2.01	0.25	1.71	0.31
3	1.93	0.20	1.60	0.10
4	1.99	0.06	1.97	0.46
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.74	-0.31	0.64	-0.45
2	0.85	-0.17	0.70	-0.35
3	0.81	-0.21	0.66	-0.42
4	0.84	-0.18	0.81	-0.21

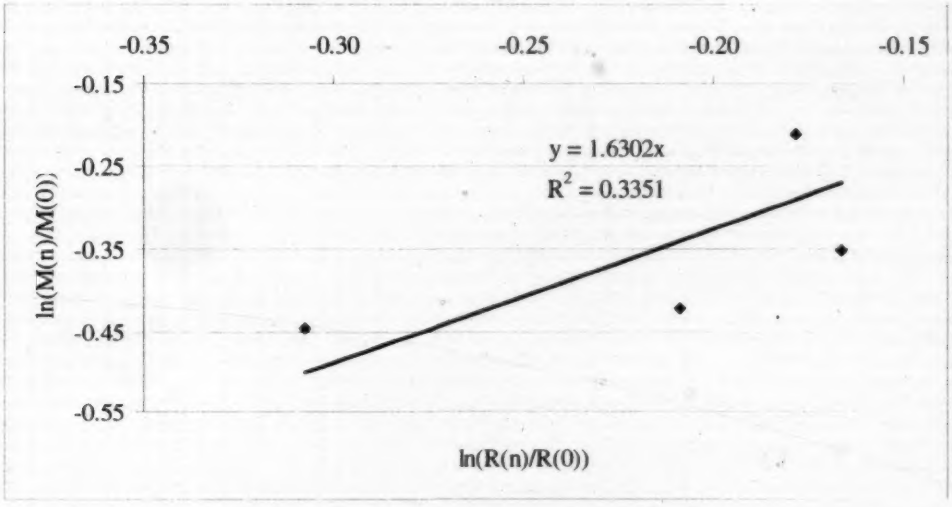

Figure 7.14. Competitive Kinetics Results, Replicate 1, Run 7: pH 4, O_3/H_2O_2 = 1:2

m = 1.6302
$k_{O3\text{-}E1} = 1.55 \times 10^3\ M^{-1}s^{-1}$

Table 7.69. Part I - Replicate 1, Run 7.2 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 1:2

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.75	0.37	1.92	0.32
1	2.00	0.28	0.73	0.08
2	2.08	0.04	1.01	0.03
3	1.86	0.14	1.17	0.02
4	1.90	0.16	1.59	0.14
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	1.14	0.13	0.38	-0.97
2	1.19	0.17	0.53	-0.64
3	1.06	0.06	0.61	-0.50
4	1.09	0.08	0.83	-0.19

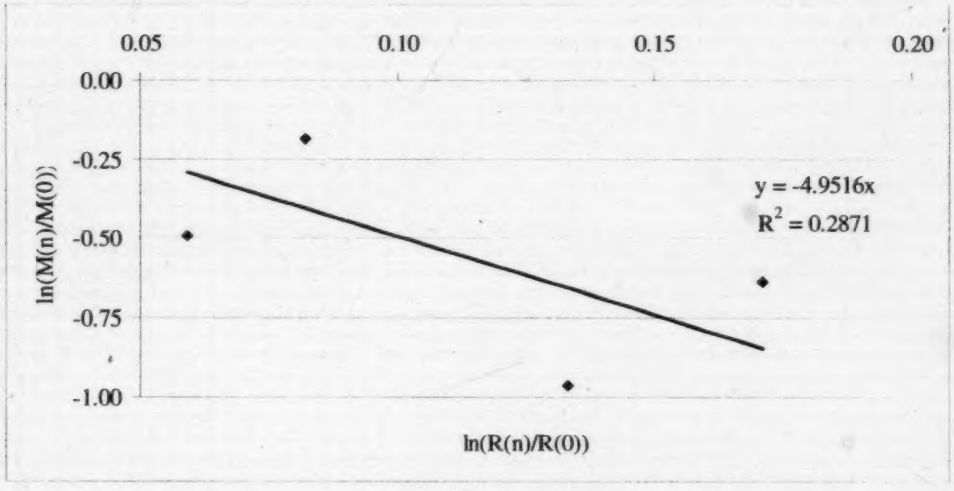

Figure 7.15. Competitive Kinetics Results, Replicate 1, Run 7.2: pH 4, O_3/H_2O_2 = 1:2

m = -4.9516
$k_{O3\text{-}E1} = -4.72 \times 10^3\ M^{-1}s^{-1}$

Table 7.70. Part I - Replicate 1, Run 7.3 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 1:2

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.21	0.06	1.48	0.12
1	1.20	0.14	0.63	0.05
2	1.35	0.15	0.59	0.11
3	1.28	0.17	0.92	0.10
4	1.20	0.25	1.26	0.13
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.99	-0.01	0.43	-0.85
2	1.11	0.11	0.40	-0.92
3	1.05	0.05	0.62	-0.47
4	0.99	-0.01	0.85	-0.16

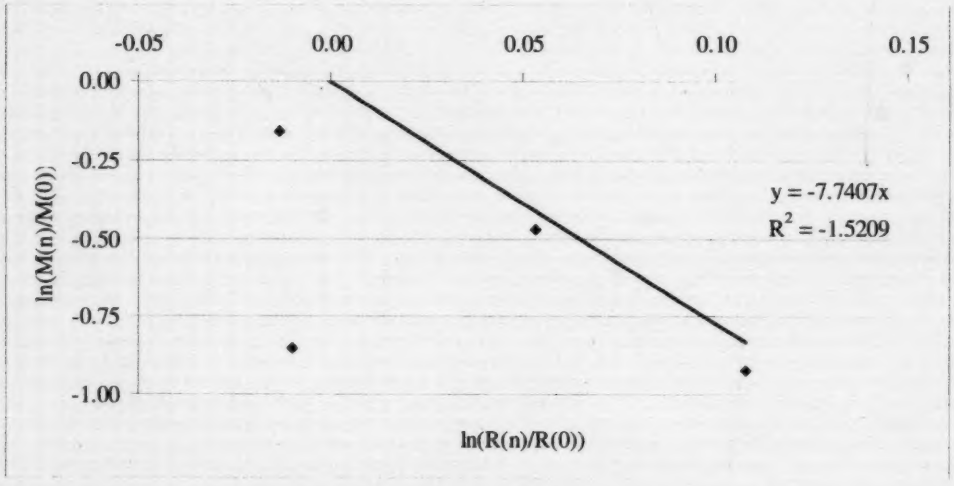

Figure 7.16. Competitive Kinetics Results, Replicate 1, Run 7.3: pH 4, O_3/H_2O_2 = 1:2

m = -7.7407
$k_{O3\text{-}E1} = -7.38 \times 10^3\ M^{-1}s^{-1}$

Table 7.71. Part I - Replicate 1, Run 7.4 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 1:2

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.61	0.09	2.50	0.13
1	1.71	0.28	1.25	0.14
2	1.64	0.02	1.51	0.04
3	1.57	0.19	1.76	0.36
4	1.61	0.15	2.19	0.23
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	1.06	0.06	0.50	-0.69
2	1.02	0.02	0.60	-0.50
3	0.98	-0.03	0.70	-0.35
4	1.00	0.00	0.88	-0.13

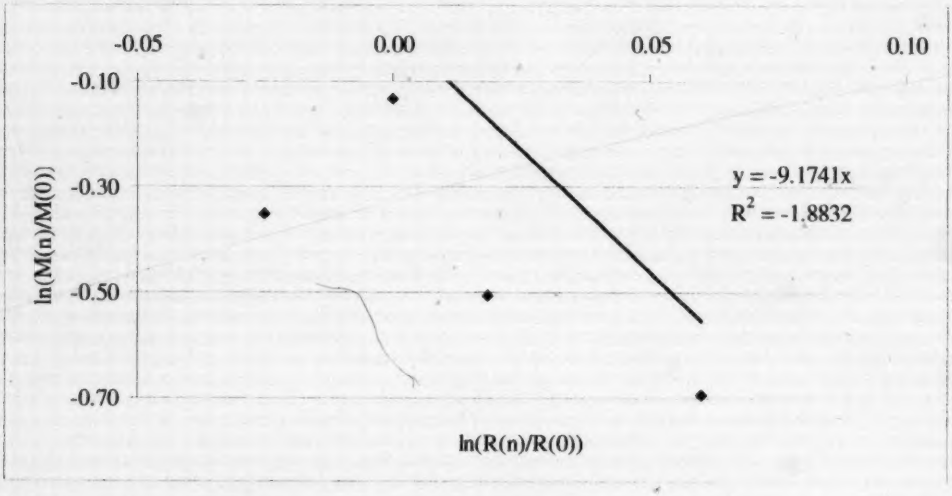

Figure 7.17. Competitive Kinetics Results, Replicate 1, Run 7.4: pH 4, O_3/H_2O_2 = 1:2

m = -9.1741
$k_{O3\text{-}E1} = -8.75 \times 10^3\ M^{-1}s^{-1}$

Table 7.72. Part I - Replicate 1, Run 7.5 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 1:2

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.69	0.13	2.95	0.46
1	1.49	0.13	1.36	0.14
2	1.48	0.09	1.66	0.24
3	1.51	0.09	2.01	0.10
4	1.63	0.16	2.49	0.24
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.88	-0.13	0.46	-0.77
2	0.88	-0.13	0.56	-0.57
3	0.89	-0.11	0.68	-0.38
4	0.96	-0.04	0.84	-0.17

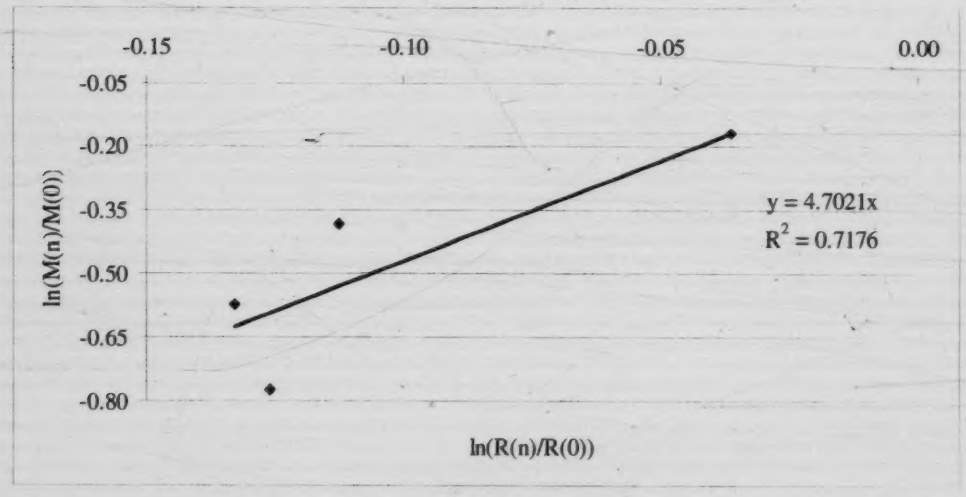

Figure 7.18. Competitive Kinetics Results, Replicate 1, Run 7.5: pH 4, O_3/H_2O_2 = 1:2

m = 4.7021
$k_{O3\text{-}E1} = 4.48 \times 10^3\ M^{-1}s^{-1}$

Table 7.73. Part I - Replicate 1, Run 8 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 4:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.31	0.01	2.28	0.12
1	1.54	0.16	0.19	0.05
2	1.66	0.00	0.72	0.17
3	2.15	0.24	1.68	0.26
4	2.01	0.34	2.34	0.42
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.67	-0.41	0.09	-2.46
2	0.72	-0.33	0.32	-1.15
3	0.93	-0.07	0.74	-0.31
4	0.87	-0.14	1.03	0.03

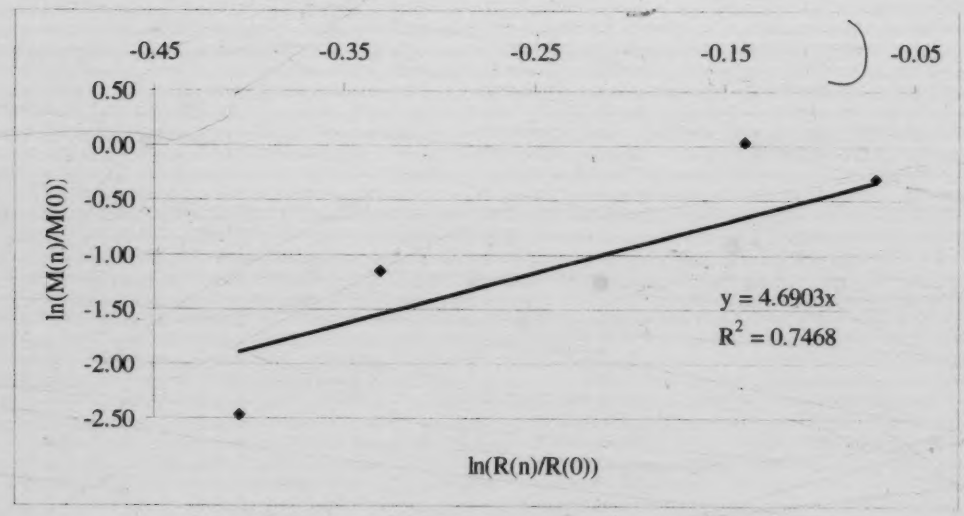

Figure 7.19. Competitive Kinetics Results, Replicate 1, Run 8: pH 4, O_3/H_2O_2 = 4:1

m = 4.6903
$k_{O3\text{-}E1} = 4.47 \times 10^2\ M^{-1}s^{-1}$

Table 7.74. Part I - Replicate 1, Run 8.2 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 4:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.82	0.35	1.52	0.21
1	1.38	0.17	0.03	0.01
2	1.46	0.06	0.09	0.01
3	1.62	0.48	0.80	0.22
4	1.99	0.42	1.35	0.06
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.75	-0.28	0.019	-3.97
2	0.80	-0.22	0.06	-2.82
3	0.89	-0.12	0.53	-0.64
4	1.09	0.09	0.89	-0.12

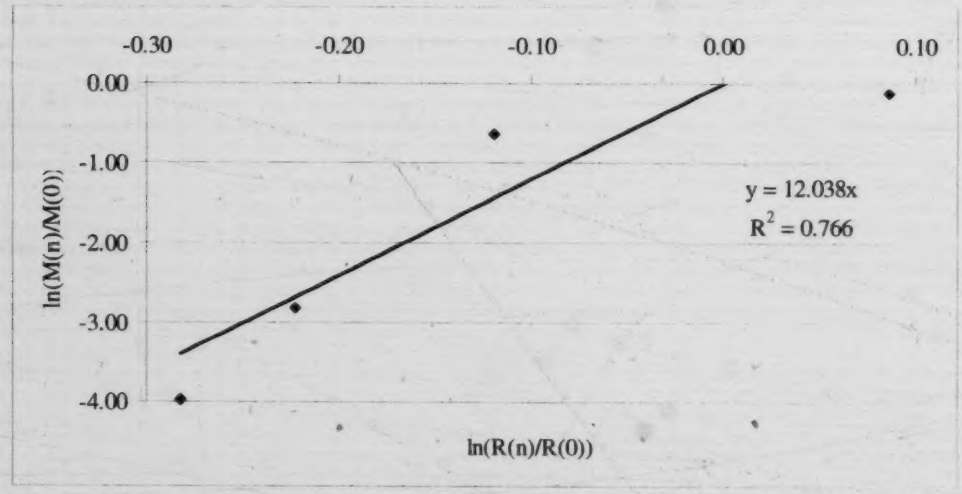

Figure 7.20. Competitive Kinetics Results, Replicate 1, Run 8.2: pH 4, O_3/H_2O_2 = 4:1

m = 12.038
$k_{O3\text{-}E1} = 1.15 \times 10^4\ M^{-1}s^{-1}$

Table 7.75. Part I - Replicate 1, Run 9 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 1:2

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.18	0.22	2.78	0.25
1	1.28	0.27	1.62	0.42
2	1.54	0.10	1.77	0.43
3	1.66	0.08	2.36	0.10
4	1.91	0.18	2.62	0.24

Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.59	-0.53	0.58	-0.54
2	0.70	-0.35	0.64	-0.45
3	0.76	-0.27	0.85	-0.17
4	0.87	-0.14	0.94	-0.06

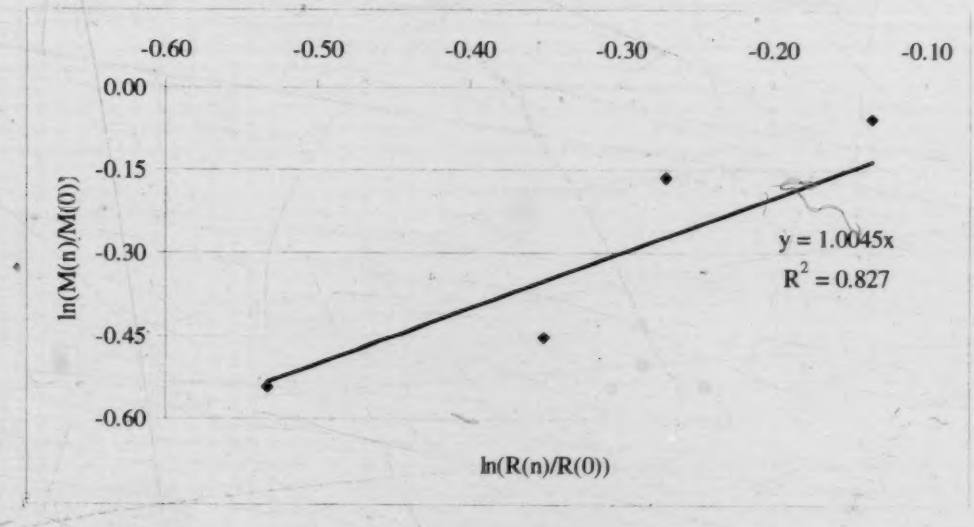

Figure 7.21. Competitive Kinetics Results, Replicate 1, Run 9: pH 8.5, O_3/H_2O_2 = 1:2

m = 1.0045
$k_{O3\text{-}E1} = 1.68 \times 10^7\ M^{-1}s^{-1}$

Table 7.76. Part I - Replicate 2, Run 1 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 4:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.37	0.29	1.79	0.38
1	0.35	0.05	0.21	0.01
2	0.43	0.08	0.73	0.15
3	0.95	0.15	1.30	0.15
4	1.14	0.23	1.35	0.22
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.26	-1.37	0.12	-2.14
2	0.31	-1.17	0.41	-0.90
3	0.69	-0.37	0.73	-0.32
4	0.83	-0.18	0.75	-0.28

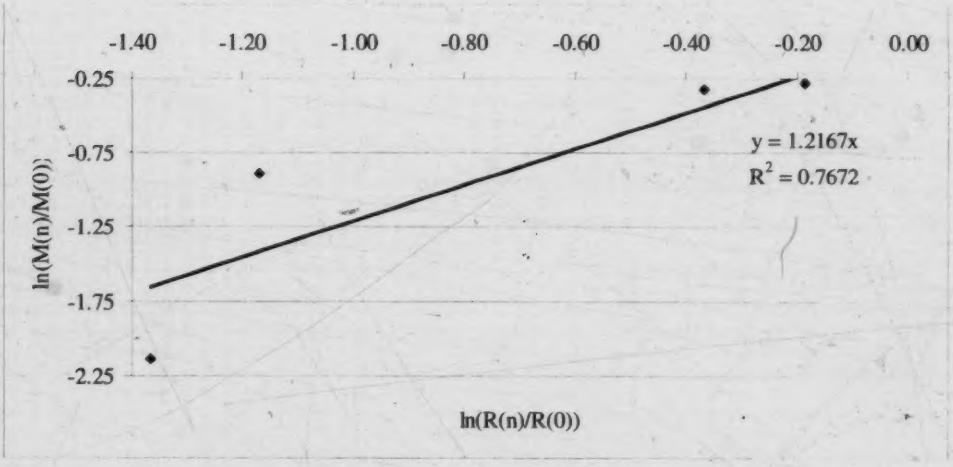

Figure 7.22. Competitive Kinetics Results, Replicate 2, Run 1: pH 8.5, O_3/H_2O_2 = 4:1

m = 1.2167
$k_{O3\text{-}E1} = 2.03 \times 10^7\ M^{-1}s^{-1}$

Table 7.77. Part I - Replicate 2, Run 2 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 2:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.09	0.07	1.72	0.03
2	0.60	0.01	0.68	0.15
3	0.73	0.02	0.87	0.14
4	0.89	0.09	1.27	0.13
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
2	0.55	-0.60	0.40	-0.93
3	0.67	-0.40	0.51	-0.68
4	0.82	-0.20	0.74	-0.30

Sample 1 excluded because didn't receive full ozone dose during test.

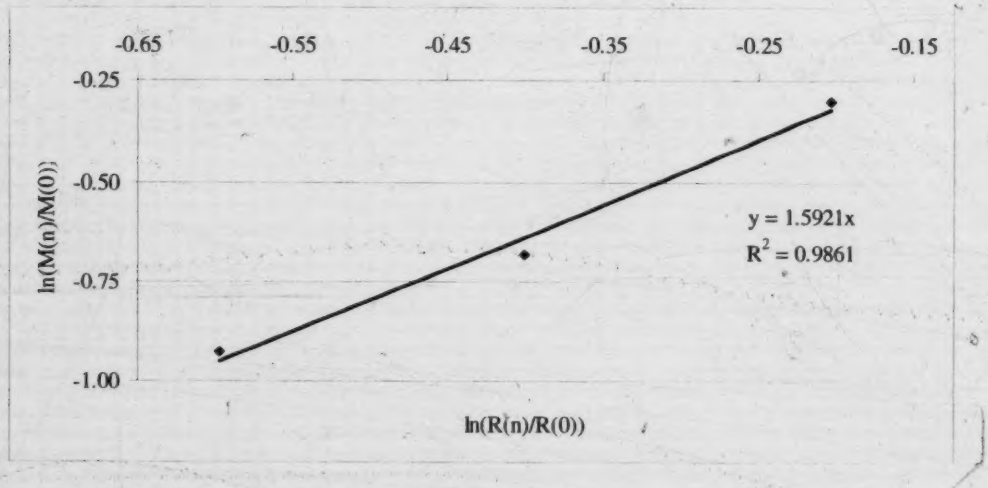

Figure 7.23. Competitive Kinetics Results, Replicate 2, Run 2: pH 7, O_3/H_2O_2 = 2:1

m = 1.5921
$k_{O3\text{-}E1} = 8.73 \times 10^5\ M^{-1}s^{-1}$

Table 7.78. Part I - Replicate 2, Run 3 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 1:2

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.13	0.23	1.64	0.02
1	0.98	0.13	0.43	0.16
2	1.09	0.17	0.63	0.01
3	0.97	0.05	1.01	0.09
4	0.99	0.01	1.47	0.12
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.87	-0.14	0.26	-1.34
2	0.96	-0.04	0.38	-0.96
3	0.86	-0.15	0.62	-0.48
4	0.88	-0.13	0.90	-0.11

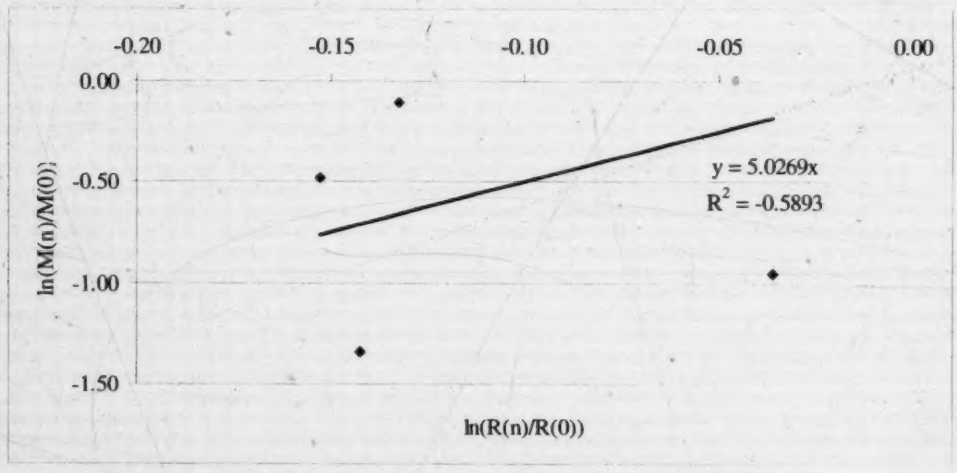

Figure 7.24. Competitive Kinetics Results, Replicate 2, Run 3: pH 4, O_3/H_2O_2 = 1:2

m = 5.0269
$k_{O3\text{-}E1} = 4.79 \times 10^3\ M^{-1}s^{-1}$

Table 7.79. Part I - Replicate 2, Run 3.2 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 1:2

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	0.91	0.05	1.60	0.03
1	0.60	0.05	0.43	0.04
2	0.64	0.07	0.63	0.13
3	0.75	0.09	0.92	0.17
4	0.91	0.08	1.22	0.21
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.66	-0.41	0.27	-1.31
2	0.71	-0.35	0.39	-0.93
3	0.83	-0.19	0.58	-0.55
4	1.00	0.00	0.76	-0.27

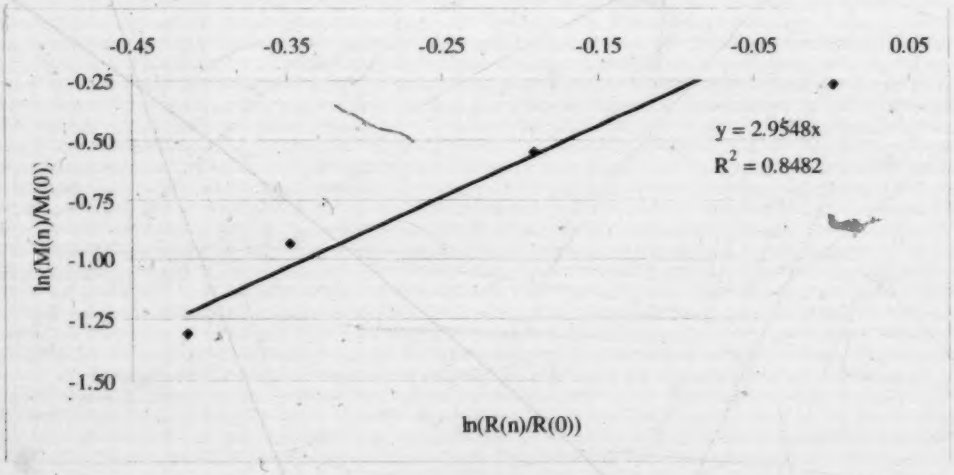

Figure 7.25. Competitive Kinetics Results, Replicate 2, Run 3.2: pH 4, O_3/H_2O_2 = 1:2

m = 2.9548
$k_{O3\text{-}E1} = 2.82 \times 10^3\ M^{-1}s^{-1}$

Table 7.80. Part I - Replicate 2, Run 4 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 4:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sam	Average	Standard Deviation	Average	Standard Deviation
Con	1.93	0.07	2.27	0.11
2	1.49	0.20	0.28	0.06
3	1.88	0.08	1.26	0.10
4	1.86	0.20	1.70	0.14
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
2	0.77	-0.26	0.12	-2.09
3	0.97	-0.03	0.56	-0.59
4	0.96	-0.04	0.75	-0.29

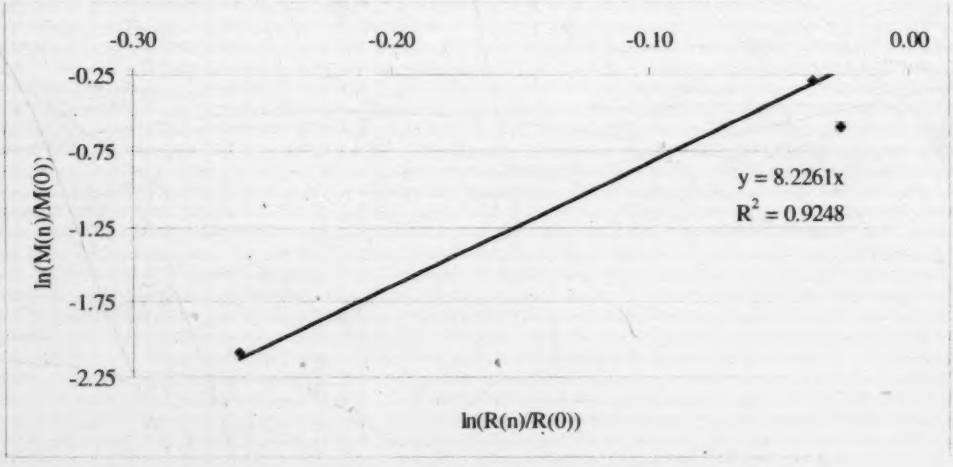

Figure 7.26. Competitive Kinetics Results, Replicate 2, Run 4: pH 4, O_3/H_2O_2 = 4:1

m = 8.2261
$k_{O3\text{-}E1} = 7.84 \times 10^3\ M^{-1}s^{-1}$

Table 7.81. Part I - Replicate 2, Run 5 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 2:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.69	0.33	2.56	0.41
1	2.11	0.29	0.19	0.02
2	2.28	0.02	0.63	0.04
3	2.32	0.06	1.22	0.00
4	2.52	0.22	1.74	0.12
Sample	R(n)/R(0)	ln(Rn/R0)	M(n)/M(0)	ln(Mn/M0)
1	0.78	-0.24	0.07	-2.60
2	0.85	-0.17	0.25	-1.40
3	0.86	-0.15	0.48	-0.74
4	0.94	-0.07	0.68	-0.39

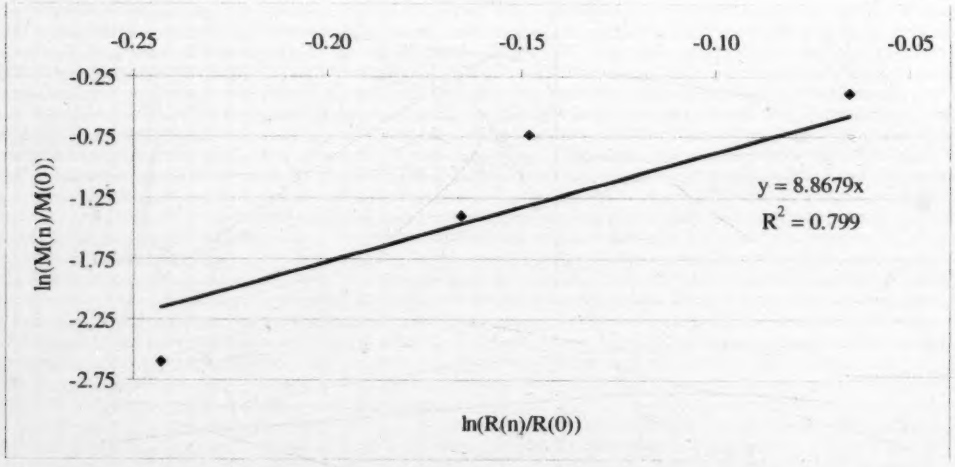

Figure 7.27. Competitive Kinetics Results, Replicate 2, Run 5: pH 4, O_3/H_2O_2 = 2:1

m = 8.8679
$k_{O3\text{-}E1} = 8.46 \times 10^3\ M^{-1}s^{-1}$

Table 7.82. Part I - Replicate 2, Run 6 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 1:2

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.84	0.13	2.85	0.01
1	1.17	0.03	1.75	0.19
2	1.41	0.16	2.23	0.17
3	1.39	0.15	2.02	0.30
4	1.58	0.22	2.41	0.11
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.64	-0.45	0.61	-0.49
2	0.77	-0.27	0.78	-0.25
3	0.76	-0.28	0.71	-0.34
4	0.86	-0.15	0.85	-0.17

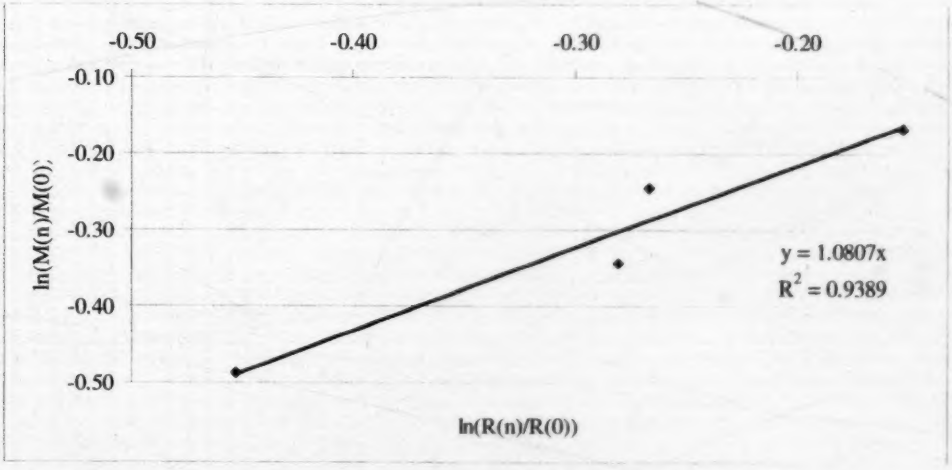

Figure 7.28. Competitive Kinetics Results, Replicate 2, Run 6: pH 8.5, O_3/H_2O_2 = 1:2

m = 1.0807
$k_{O3\text{-}E1} = 1.80 \times 10^7\ M^{-1}s^{-1}$

Table 7.83. Part I - Replicate 2, Run 7 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 4:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.66	0.07	2.76	0.09
1	0.72	0.14	0.94	0.05
2	1.25	0.14	1.70	0.10
3	1.34	0.18	1.56	0.23
4	1.42	0.23	1.92	0.24
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.43	-0.84	0.34	-1.08
2	0.75	-0.28	0.62	-0.48
3	0.81	-0.21	0.57	-0.57
4	0.86	-0.16	0.70	-0.36

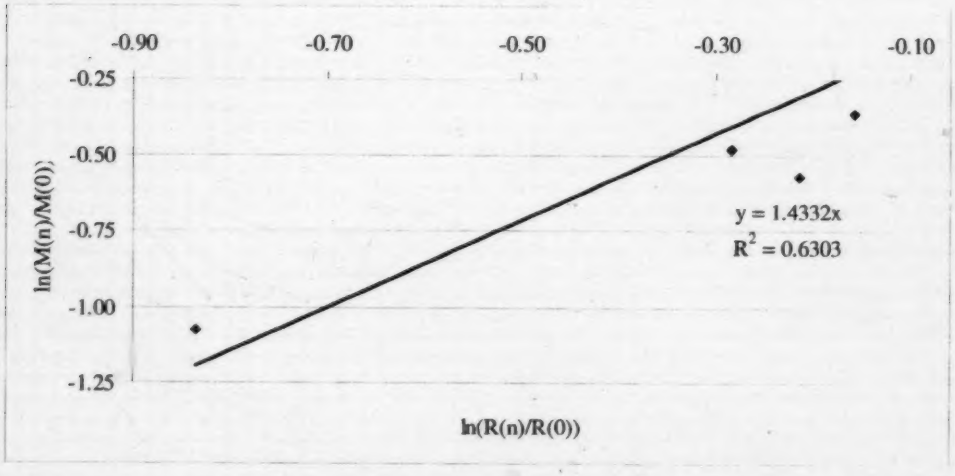

Figure 7.29. Competitive Kinetics Results, Replicate 2, Run 7: pH 7, O_3/H_2O_2 = 4:1

m = 1.4332
$k_{O3\text{-}E1} = 7.86 \times 10^5\ M^{-1}s^{-1}$

Table 7.84. Part I - Replicate 2, Run 8 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 1:2

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.75	0.40	2.89	0.43
1	1.21	0.03	1.88	0.08
2	1.35	0.27	2.07	0.24
3	1.42	0.17	2.16	0.11
4	1.43	0.07	2.32	0.16
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.69	-0.37	0.65	-0.43
2	0.77	-0.26	0.72	-0.33
3	0.81	-0.21	0.75	-0.29
4	0.82	-0.20	0.80	-0.22

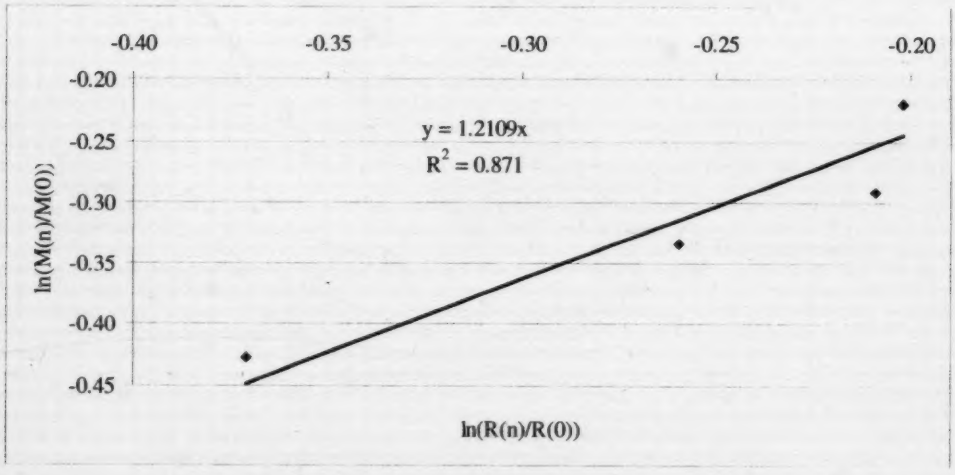

Figure 7.30. Competitive Kinetics Results, Replicate 2, Run 8: pH 7, O_3/H_2O_2 = 1:2

m = 1.2109
$k_{O3\text{-}E1} = 6.64 \times 10^5\ M^{-1}s^{-1}$

Table 7.85. Part I - Replicate 2, Run 9 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 2:1

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.71	0.11	2.90	0.13
1	0.84	0.03	1.27	0.04
2	1.16	0.14	1.72	0.16
3	1.22	0.03	1.82	0.03
4	1.44	0.02	2.19	0.15
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.49	-0.71	0.44	-0.83
2	0.68	-0.39	0.59	-0.52
3	0.71	-0.34	0.63	-0.46
4	0.84	-0.17	0.76	-0.28

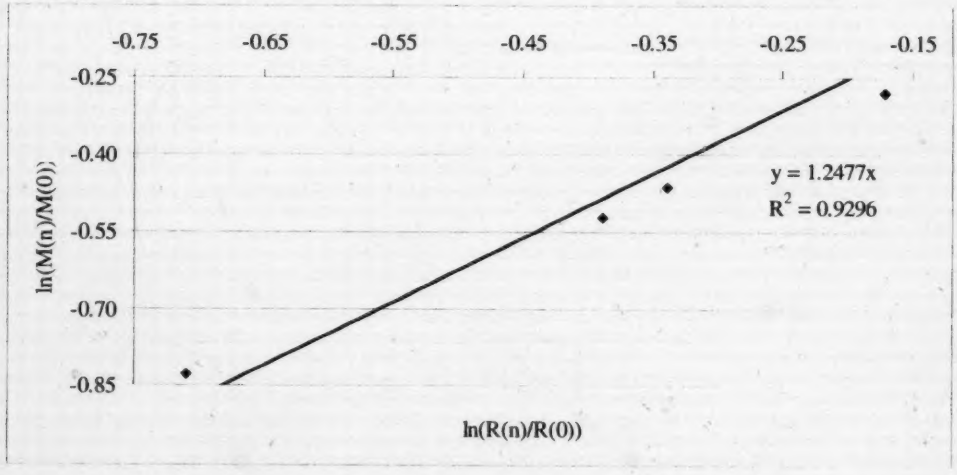

Figure 7.31. Competitive Kinetics Results, Replicate 2, Run 9: pH 8.5, O_3/H_2O_2 = 2:1

m = 1.2477
$k_{O3\text{-}E1} = 2.08 \times 10^7\ M^{-1}s^{-1}$

Table 7.86. Part I - Control Run Rate Constant Calculations: pH 7, O_3/H_2O_2 = 2:1, no TBA

	Phenol Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.85	0.23	2.63	0.22
1	1.09	0.07	1.56	0.15
3	1.36	0.11	2.02	0.16
4	1.42	0.15	2.03	0.20
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.59	-0.53	0.59	-0.52
3	0.73	-0.31	0.77	-0.27
4	0.77	-0.26	0.77	-0.26

Sample 2 excluded because didn't receive full ozone dose

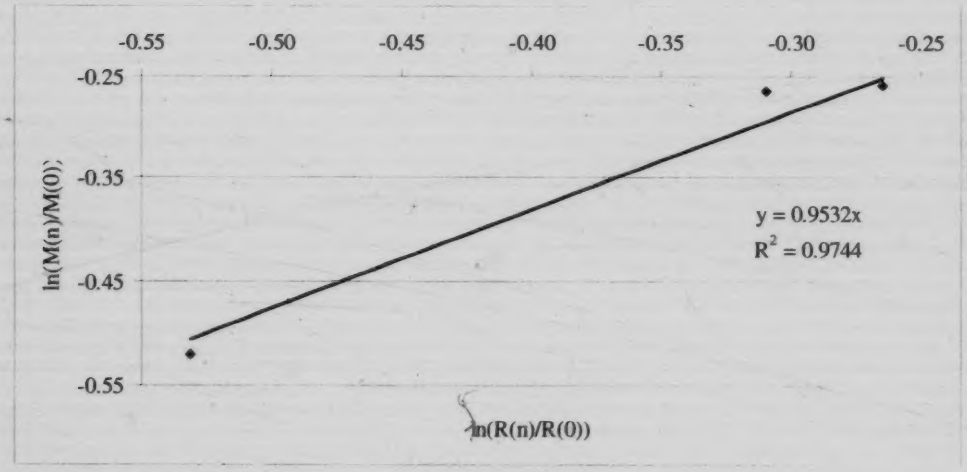

Figure 7.32. Competitive Kinetics Results, Control Run, no TBA: pH 7, O_3/H_2O_2 = 2:1

m = 0.9532
$k_{O3\text{-}E1} = 5.23 \times 10^5\ M^{-1}s^{-1}$

Appendix D: HPLC standards and method description, Part II (·OH experiments)

HPLC Method Description

E1 standards prepared in methanol.

Gradient: isocratic, 50% acetonitrile, 50% Elga water (both filtered)
Column: C18 5 um Phenomenex column, 250 mm ×4.6 mm
Injection volume: 20 uL
Run time: 15 min. (Shortened to 14 min., then 13 min., then back to 14 min. again during experiments)

Standards done April 23, 2007.

Table 7.87. E1 Standards and HPLC Analysis for ·OH Experiments.

Concentration	Replicate	Peak Area	Retention Time (min.)	Standard Deviation*
5 µM	1	11998	11.817	442.9
	2	11404	11.817	
	3	12270	11.85	
	Average	**11891**	**11.828**	
3.5 µM	1	8246	11.8	183.6
	2	8554	11.8	
	3	8227	11.833	
	Average	**8342**	**11.811**	
2 µM	1	4719	11.8	308.5
	2	4590	11.8	
	3	4132	11.833	
	Average	**4480**	**11.811**	
1 µM	1	1978	11.817	162.2
	2	2035	11.783	
	3	1730	11.817	
	Average	**1914**	**11.806**	

*Standard deviation calculated using peak area counts.

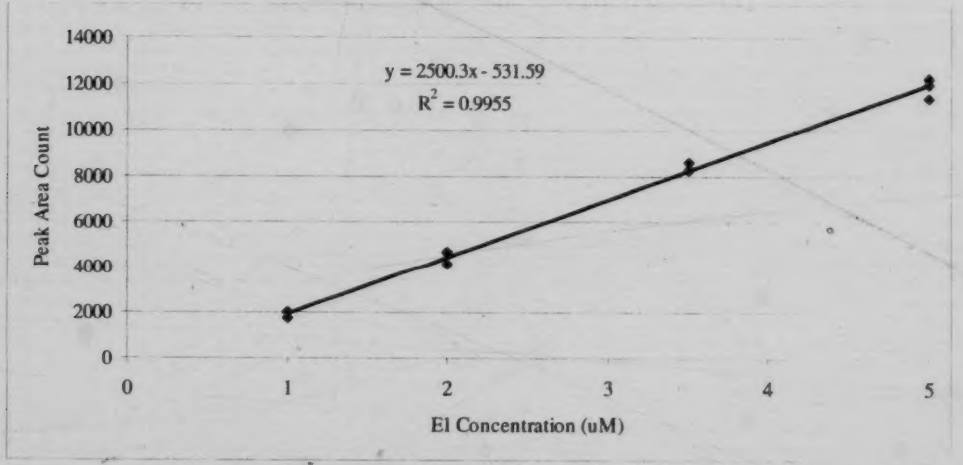

Figure 7.33. E1 Concentration Standard Curve

Acetophenone (Reference Compounds) Standards

HPLC Method Description: as above

Acetophenone standards prepared in methanol.

Standards done on April 20th, 2007

Table 7.88. Acetophenone Standards and HPLC Analysis for ·OH Experiments.

Concentration	Replicate	Peak Area	Retention Time	Standard Deviation
5 μM	1	5296	6.983	193.4
	2	5633	6.95	
	3	5629	6.95	
	Average	**5519**	**6.961**	
3.5 μM	1	4362	6.95	171.1
	2	4075	6.95	
	3	4057	6.95	
	Average	**4165**	**6.950**	
2.5 μM	1	3128	6.95	188.3
	2	2706	6.95	
	3	3061	6.95	
	4	2901	6.95	
	5	2737	6.95	
	Average	**2907**	**6.950**	
1 μM	1	885	6.95	39.4
	2	905	6.95	
	3	961	6.933	
	Average	**917**	**6.944**	

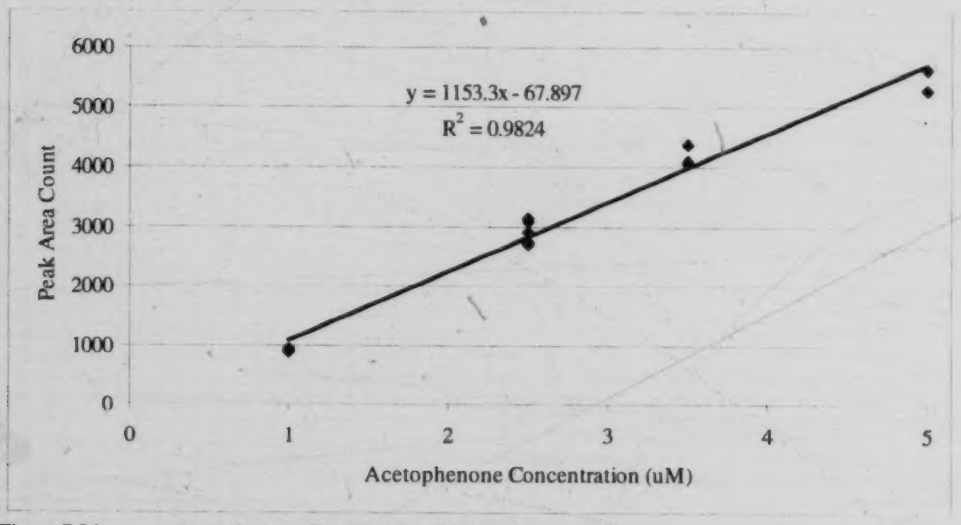

Figure 7.34. Acetophenone Concentration Standard Curve

Appendix E: HPLC run results, Part II (·OH experiments)

Table 7.89. Part II - Replicate 1, Run 1 Results: pH 4, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Acetophenone							
Control	1	931	7.083	1.73	1.89	0.27	14.44
	2	852	7.1	1.60			
	3	1198	7.1	2.20			
	4	1099	7.1	2.02			
3	1	701	7.083	1.33	1.71	0.37	21.38
	2	882	7.083	1.65			
	3	1207	7.1	2.21			
	4	881	7.1	1.65			
4	1	908	7.083	1.69	2.01	0.28	13.94
	2	1005	7.1	1.86			
	3	1191	7.117	2.18			
	4	1256	7.1	2.30			
E1							
Control	1	2061	12.117	2.07	2.22	0.19	8.43
	2	2027	12.117	2.05			
	3	2499	12.15	2.42			
	4	2380	12.15	2.33			
3	1	655	12.067	0.95	1.18	0.22	19.08
	2	859	12.117	1.11			
	3	1325	12.133	1.49			
	4	920	12.15	1.16			
4	1	1475	12.083	1.61	1.64	0.03	1.82
	2	1523	12.117	1.64			
	3	1564	12.133	1.68			
	4	1505	12.167	1.63			

Samples 1 and 2 not included in analysis because initial runs showed no E1

Table 7.90. Part II - Replicate 1, Run 1.2 Results: pH 4, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Acetophenone							
Control	1 2	2858 3070	7.183 7.767	5.07 5.44	5.26	0.26	4.94
1	1 2 3	2904 2962 2719	7.2 7.183 7.183	5.15 5.25 4.83	5.08	0.22	4.33
2	1 2 3 4	2777 2824 2864 2889	7.2 7.183 7.183 7.183	4.93 5.01 5.08 5.13	5.04	0.08	1.68
3	1 2	2978 2871	7.2 7.183	5.28 5.10	5.19	0.13	2.53
4	1 2 3	2793 3110 2978	7.183 7.183 7.833	4.96 5.51 5.28	5.25	0.28	5.26
E1							
Control	1 2	5306 5497	12.383 12.367	4.67 4.82	4.75	0.11	2.28
1	1 2 3	2592 2685 2378	12.417 12.35 12.383	2.50 2.57 2.33	2.47	0.13	5.11
2	1 2 3 4	2971 3246 3247 3278	12.4 12.383 12.367 12.4	2.80 3.02 3.02 3.05	2.97	0.12	3.87
3	1 2	4212 4041	12.383 12.367	3.79 3.66	3.73	0.10	2.60
4	1 2 3	4921 5101 4829	12.4 12.383 12.383	4.36 4.51 4.29	4.39	0.11	2.52

Table 7.91. Part II - Replicate 1, Run 2 Acetophenone Results: pH 7, $O_3/H_2O_2 = 4:1$

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1128	7.117	2.07	2.10	0.05	2.17
	2	1174	7.117	2.15			
	3	1129	7.117	2.08			
1	1	741	7.117	1.40	1.39	0.01	0.88
	2	731	7.1	1.39			
2	1	738	7.117	1.40	1.64	0.31	18.82
	2	1023	7.117	1.89			
	3	1044	7.117	1.93			
	4	713	7.1	1.35			
3	1	1053	7.117	1.94	1.94	0.07	3.75
	2	1065	7.11	1.96			
	3	994	7.117	1.84			
	4	1094	7.117	2.01			
4	1	1068	7.117	1.97	2.06	0.14	6.70
	2	1167	7.117	2.14			
	3	1208	7.117	2.21			
	4	1040	7.1	1.92			

Table 7.92. Part II - Replicate 1, Run 2 E1 Results: pH 7, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	2502	12.167	2.43	2.51	0.10	4.09
	2	2751	12.183	2.63			
	3	2572	12.167	2.48			
1	1	904	12.167	1.15	1.17	0.03	2.23
	2	950	12.15	1.19			
2	1	949	12.183	1.18	1.31	0.13	10.21
	2	1074	12.15	1.28			
	3	1340	12.167	1.50			
	4	1050	12.15	1.27			
3	1	2462	12.183	2.39	2.16	0.17	7.78
	2	2005	12.15	2.03			
	3	2029	12.167	2.05			
	4	2184	12.183	2.17			
4	1	2163	12.167	2.16	2.13	0.09	4.37
	2	2243	12.167	2.22			
	3	2168	12.183	2.16			
	4	1970	12.167	2.00			

Table 7.93. Part II - Replicate 1, Run 3 Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Acetophenone							
Control	1 2 3	1120 952 986	7.167 7.167 7.183	2.06 1.77 1.83	1.89	0.15	8.17
1	1 2 3	788 972 915	7.15 7.183 7.183	1.48 1.80 1.70	1.66	0.16	9.82
2	1 2	930 912	7.167 7.167	1.73 1.70	1.71	0.02	1.29
3	1 2	1006 1086	7.167 7.167	1.86 2.00	1.93	0.10	5.08
4	1 2 3	1028 924 1191	7.167 7.167 7.183	1.90 1.72 2.18	1.93	0.23	12.06
E1							
Control	1 2 3	2703 2305 2411	12.317 12.333 12.367	2.59 2.27 2.35	2.40	0.16	6.86
1	1 2 3	1109 1404 1269	12.3 12.333 12.367	1.31 1.55 1.44	1.43	0.12	8.24
2	1 2	1560 1451	12.283 12.317	1.67 1.59	1.63	0.06	3.78
3	1 2	2031 1985	12.317 12.317	2.05 2.01	2.03	0.03	1.28
4	1 2 3	2497 2089 2146	12.317 12.317 12.35	2.42 2.10 2.14	2.22	0.18	7.96

Table 7.94. Part II - Replicate 1, Run 4 Acetophenone Results: pH 8.5, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	744	7.167	1.41	1.59	0.14	9.01
	2	834	7.15	1.56			
	3	866	7.167	1.62			
	4	943	12.35	1.75			
1	[redacted]				1.22	0.02	1.50
	2	636	7.167	1.22			
	3	645	7.15	1.24			
	4	624	7.183	1.20			
2	1	594	7.15	1.15	1.24	0.07	5.32
	2	676	7.15	1.29			
	3	640	7.15	1.23			
	4	672	7.183	1.28			
3	1	604	7.15	1.17	1.31	0.15	11.12
	2	735	7.15	1.39			
	3	635	7.167	1.22			
	4	784	7.183	1.48			
4	1	789	7.167	1.49	1.45	0.05	3.38
	2	749	7.15	1.42			

[redacted]

Table 7.95. Part II - Replicate 1, Run 4 E1 Results: pH 8.5, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	2569	12.25	2.48	2.76	0.22	8.07
	2	2825	12.25	2.68			
	3	3104	12.283	2.91			
	4	3178	12.35	2.97			
1	1	899	12.233	1.14	1.31	0.08	6.26
	2	989	12.283	1.22			
	3	1133	12.25	1.33			
	4	1187	12.283	1.37			
2	1	1323	12.233	1.48	1.66	0.17	10.38
	2	1483	12.283	1.61			
	3	1838	12.233	1.90			
	4	1531	12.317	1.65			
3	1	1687	12.25	1.77	2.02	0.19	9.18
	2	2247	12.25	2.22			
	3	1992	12.267	2.02			
	4	2050	12.317	2.07			
4	1	2459	12.25	2.39	2.36	0.04	1.87
	2	2381	12.25	2.33			

Replicate identified as outlier using Q-test

Table 7.96. Part II - Replicate 1, Run 5 Acetophenone Results: pH 4, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1483	7.133	2.69	2.51	0.08	3.04
	2	1401	7.133	2.55			
	3	1332	7.133	2.43			
	4	1414	7.133	2.57			
1	1	1025	7.133	1.90	2.13	0.18	8.50
	2	1140	7.133	2.09			
	3	1263	7.133	2.31			
	4	1220	7.133	2.23			
2	1	1126	7.133	2.07	2.28	0.14	6.27
	2	1250	7.133	2.29			
	3	1330	7.133	2.42			
	4	1165	7.133	2.14			
3	1	1145	7.133	2.10	2.24	0.12	5.50
	2	1185	7.133	2.17			
	3	1304	7.133	2.38			
	4	1255	7.15	2.29			
4	1	1382	7.133	2.51	2.45	0.02	0.92
	2	1333	12.217	2.43			
	3	1359	7.133	2.47			
	4	1344	7.133	2.45			

Replicate identified as outlier, using Q-test

Sketchy - chromatogram very noisy

Table 7.97. Part II - Replicate 1, Run 5 E1 Results: pH 4, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	[redacted]				3.08	0.01	0.37
	2	3308	12.217	3.07			
	3	3317	12.217	3.08			
	4	3336	12.233	3.09			
1	1	241	12.217	0.62	0.67	0.04	6.67
	2	282	12.25	0.65			
	3	330	12.183	0.69			
	4	369	12.233	0.72			
2	[redacted]				1.36	0.04	2.71
	2	1175	12.233	1.37			
	3	1118	12.233	1.32			
	4	1209	12.217	1.39			
3	1	1345	12.267	1.50	1.85	0.26	14.01
	2	1768	12.217	1.84			
	3	2121	12.217	2.12			
	4	1870	12.233	1.92			
4	[redacted]				3.16	0.09	2.99
	2	3327	12.217	3.09			
	3	3549	12.217	3.26			
	4	3368	12.217	3.12			

sketchy - chromatogram very noisy
double peak on E1 for 3-1

Table 7.98. Part II - Replicate 1, Run 6 Acetophenone Results: pH 8.5, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1063	6.917	1.96	2.07	0.08	3.66
	2	1145	6.917	2.10			
	3	1159	6.917	2.13			
	4	1144	11.467	2.10			
1	1	876	6.933	1.64	1.73	0.07	4.29
	2	949	6.917	1.76			
	3	974	6.917	1.81			
	4	913	6.917	1.70			
2	1	1030	6.9	1.90	1.85	0.05	2.69
	2	995	6.917	1.84			
	3	973	6.917	1.81			
	4	1268	6.95	2.32			
3	1	1064	6.917	1.96	1.97	0.05	2.31
	2	1095	11.467	2.02			
	3	1034	6.917	1.91			
	4	1081	6.917	1.99			
4	1	1045	6.917	1.93	1.90	0.10	5.25
	2	972	6.917	1.80			
	3	988	6.917	1.83			
	4	1098	6.917	2.02			

sketchy - chromatogram very noisy

Table 7.99. Part II - Replicate 1, Run 6 E1 Results: pH 8.5, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	3061	11.483	2.87	2.80	0.14	5.10
	2	3164	11.483	2.96			
	3	2894	11.467	2.74			
	4	2760	11.467	2.63			
1	1	1814	11.5	1.88	1.91	0.12	6.41
	2	1830	11.483	1.89			
	3	2061	11.5	2.07			
	4	1696	11.45	1.78			
2	1	1948	11.467	1.98	1.93	0.12	6.32
	2	1703	11.483	1.79			
	3	1982	11.483	2.01			
	4	2537	11.5	2.45			
3	1	2120	11.467	2.12	2.28	0.18	8.07
	2	2612	11.467	2.51			
	3	2146	11.483	2.14			
	4	2374	11.483	2.32			
4	1	2619	11.467	2.52	2.58	0.12	4.68
	2	2530	11.483	2.45			
	3	2863	11.467	2.72			
	4	2780	11.483	2.65			

sketchy - chromatogram very noisy

Table 7.100. Part II - Replicate 1, Run 6.2 Acetophenone Results: pH 8.5, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	3132	7.183	5.55	5.56	0.01	0.22
	2	3142	7.183	5.57			
1	1	2572	7.2	4.58	4.66	0.09	1.84
	2	2619	7.183	4.66			
	3	2671	7.183	4.75			
2	1	2551	7.183	4.54	5.00	0.33	6.52
	2	2842	7.183	5.05			
	3	2876	7.167	5.11			
	4	2994	7.167	5.31			
3	1	2890	7.183	5.13	5.20	0.07	1.31
	2	2968	7.183	5.26			
	3	2938	7.183	5.21			
4	1	2697	7.183	4.79	5.49	0.17	3.17
	2	3158	7.183	5.59			
	3	3149	7.183	5.58			
	4	2980	7.167	5.29			

sketchy-taken out

Table 7.101. Part II - Replicate 1, Run 6.2 E1 Results: pH 8.5, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	5962	12.333	5.19	5.13	0.09	1.66
	2	5811	12.35	5.07			
1	1	4061	12.367	3.67	3.75	0.08	2.07
	2	4168	12.333	3.76			
	3	4255	12.35	3.83			
2	1	4110	12.367	3.71	3.86	0.13	3.49
	2	4271	12.317	3.84			
	3	4516	12.35	4.04			
	4	4257	12.3	3.83			
3	1	4272	12.35	3.84	4.01	0.19	4.65
	2	4731	12.333	4.21			
	3	4431	12.317	3.97			
4	1	4789	12.3	4.26	4.73	0.20	4.27
	2	5677	12.333	4.97			
	3	5221	12.3	4.60			
	4	5261	12.283	4.63			

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sketchy-taken out

Table 7.102. Part II - Replicate 1, Run 7 Acetophenone Results: pH 8.5, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1216	6.917	2.23	2.20	0.03	1.50
	2	1189	6.917	2.18			
1	1	949	6.917	1.76	1.61	0.05	3.21
	2	826	6.917	1.55			
	3	875	6.917	1.64			
	4	880	6.9	1.64			
2	1	788	6.917	1.48	1.68	0.14	8.60
	2	911	6.917	1.70			
	3	923	6.917	1.72			
	4	988	6.917	1.83			
3	1	967	6.917	1.79	1.82	0.03	1.62
	2	991	6.917	1.84			
4	1	1111	6.917	2.04	2.03	0.04	2.11
	2	1086	6.917	2.00			
	3	1079	6.917	1.99			
	4	1133	6.917	2.08			

Replicate identified as outlier, using Q-test

Table 7.103. Part II - Replicate 1, Run 7 E1 Results: pH 8.5, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	3011	11.5	2.83	2.87	0.05	1.70
	2	3097	11.483	2.90			
1	1	[redacted]			1.31	0.00	0.17
	2	1102	11.483	1.31			
	3	1098	11.483	1.30			
	4	1086	11.5	1.29			
2	1	1451	11.5	1.59	1.54	0.05	3.47
	2	1460	11.5	1.59			
	3	1350	11.467	1.51			
	4	1331	11.5	1.49			
3	1	1832	11.5	1.89	1.88	0.02	0.93
	2	1801	11.483	1.87			
4	1	2637	11.5	2.53	2.37	0.19	8.08
	2	2197	11.483	2.18			
	3	2263	11.5	2.24			
	4	2648	11.5	2.54			

[redacted]

Table 7.104. Part II - Replicate 1, Run 8 Acetophenone Results: pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Acetophenone							
Control	1	1640	6.95	2.96	2.96	0.02	0.60
	[redacted]						
	3	1646	6.95	2.97			
	4	1626	6.95	2.94			
1	1	1118	6.933	2.06	2.09	0.03	1.42
	2	1098	6.95	2.02			
	3	1152	6.95	2.12			
	4	1139	6.933	2.09			
2	1	1312	6.95	2.39	2.33	0.09	4.00
	2	1236	6.95	2.26			
3	1	1152	6.933	2.12	2.16	0.06	2.90
	2	1203	6.933	2.20			
4	1	1348	6.95	2.46	2.42	0.05	2.23
	2	1304	6.95	2.38			
E1							
Control	1	3132	11.567	2.93	2.98	0.13	4.22
	2	2850	11.567	2.70			
	3	3076	11.55	2.89			
	4	3372	11.583	3.12			
1	1	1291	11.567	1.46	1.46	0.01	0.69
	[redacted]						
	3	1278	11.567	1.45			
	4	1303	11.567	1.47			
2	1	2244	11.583	2.22	2.16	0.08	3.87
	2	2096	11.567	2.10			
3	1	1746	11.567	1.82	1.86	0.06	3.01
	2	1845	11.567	1.90			
4	1	2280	11.567	2.25	2.24	0.01	0.66
	2	2254	11.567	2.23			

[redacted]

Replicate identified as outlier, using Q-test

Table 7.105. Part II - Replicate 1, Run 9 Acetophenone Results: pH 7, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1215	6.967	2.22	2.26	0.05	2.28
	2	1257	6.95	2.30			
1	1	1053	6.967	1.94	2.19	0.21	9.56
	2	1309	6.95	2.39			
	3	1279	6.967	2.34			
	4	1136	6.95	2.09			
2	1	1001	6.95	1.85	2.05	0.14	7.04
	2	1179	6.95	2.16			
	3	1215	6.95	2.22			
	4	1133	6.95	2.08			
	5	1120	6.967	2.06			
	6	1201	6.95	2.20			
3	1	1096	6.95	2.02	2.21	0.14	6.28
	2	1238	6.95	2.26			
	3	1284	6.967	2.34			
	4	1204	6.95	2.21			
4	1	1142	6.95	2.10	2.19	0.21	9.72
	2	1178	6.95	2.16			
	3	1370	6.983	2.49			
	4	1261	6.95	2.30			

sketchy peaks - split

Table 7.106. Part II - Replicate 1, Run 9 E1 Results: pH 7, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	3032	11.617	2.85	2.83	0.02	0.88
	2	2988	11.6	2.82			
1	1	2188	11.617	2.18	2.14	0.08	3.58
	2	2001	11.617	2.03			
	3	2215	11.6	2.20			
	4	2156	11.6	2.15			
2	1	1928	11.633	1.97	2.04	0.07	3.32
	2	2176	11.6	2.17			
	3	2166	11.633	2.16			
	4	2035	11.583	2.05			
	5	1968	11.6	2.00			
	6	2121	11.6	2.12			
3	1	2131	11.617	2.13	2.22	0.13	6.03
	2	2122	11.6	2.12			
	3	2482	11.6	2.41			
	4	2252	11.583	2.23			
4	1	2430	11.617	2.37	2.61	0.16	6.05
	2	2813	11.6	2.68			
	3	2705	11.6	2.59			
	4	2952	11.617	2.79			

sketchy peaks - split

Table 7.107. Part II - Replicate 1, Run 9.2 Results: pH 7, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Acetophenone							
Control	1 2	3015 3069	7.167 7.167	5.35 5.44	5.39	0.07	1.23
1	1 2	2972 2818	7.167 7.167	5.27 5.00	5.14	0.19	3.68
2	1 2 3 4	2893 3090 3027 2853	7.167 7.167 7.167 7.167	5.13 5.48 5.37 5.07	5.26	0.19	3.67
3	1 2	2920 3058	7.167 7.167	5.18 5.42	5.30	0.17	3.19
4	1 2 3 4 5	3091 3151 2911 2744 3231	7.167 7.167 7.167 7.167 7.167	5.48 5.58 5.17 4.88 5.72	5.36	0.34	6.36
E1							
Control	1 2	6728 6390	12.3 12.283	5.81 5.54	5.67	0.19	3.37
1	1 2	5186 4994	12.317 12.3	4.57 4.42	4.50	0.11	2.42
2	1 2 3 4	5040 5720 5285 5210	12.3 12.283 12.283 12.3	4.46 5.00 4.65 4.59	4.68	0.23	4.95
3	1 2	5959 5783	12.3 12.283	5.19 5.05	5.12	0.10	1.94
4	1 2 3 4 5	5915 6439 5830 5436 6336	12.317 12.283 12.283 12.3 12.283	5.16 5.58 5.09 4.77 5.49	5.22	0.32	6.22

Table 7.108. Part II - Replicate 2, Run 1 Acetophenone Results: pH 7, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1476	6.967	2.68	2.48	0.22	8.70
	2	1457	6.983	2.64			
	3	1237	6.983	2.26			
	4	1269	6.95	2.32			
1	1	1170	6.967	2.15	2.08	0.10	4.60
	2	1092	6.983	2.01			
2	1	1111	6.967	2.04	2.19	0.20	8.96
	2	1230	6.967	2.25			
	3	1093	6.967	2.01			
	4	1335	6.983	2.43			
3	1	796	6.967	1.50	2.23	0.16	7.01
	2	1321	6.983	2.41			
	3	1286	6.983	2.35			
	4	1129	6.983	2.08			
	5	1307	6.983	2.38			
	6	1155	6.983	2.12			
4	1	1354	6.983	2.47	2.16	0.03	1.33
	2	1179	6.983	2.16			
	[redacted]						
	4	1193	7.033	2.19			
	5	1160	6.983	2.13			

sketchy peak - split

[redacted]

Table 7.109. Part II - Replicate 2, Run 1 E1 Results: pH 7, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	2849	11.633	2.70	2.83	0.16	5.73
	2	3273	11.683	3.04			
	3	3054	11.65	2.87			
	4	2848	11.533	2.70			
1	1	1841	11.667	1.90	1.92	0.03	1.42
	2	1889	11.65	1.94			
2	1	2547	11.65	2.46	2.37	0.12	5.19
	2	2213	11.633	2.20			
	3	2415	11.633	2.36			
	4	2529	11.65	2.45			
3	1	2304	11.633	2.27	2.46	0.03	1.03
	2	1376	11.633	1.53			
	3	2523	11.65	2.44			
	4	2553	11.667	2.47			
	5	2582	11.617	2.49			
	6	2512	11.667	2.43			
4	1	2764	11.683	2.64	2.42	0.02	0.68
	2	2505	11.667	2.43			
	3	2540	11.633	2.46			
	4	2502	11.833	2.43			
	5	2468	11.667	2.40			

sketchy peak – split

Replicate identified as outlier, using Q-test

Table 7.110. Part II - Replicate 2, Run 2 Acetophenone Results: pH 4, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	1314	6.983	2.40	2.41	0.12	5.07
	2	1370	7	2.49			
	3	1229	7	2.25			
	4	1385	7	2.52			
1	1	1131	7	2.08	2.10	0.18	8.36
	2	1009		1.87			
	3	1188	7.017	2.18			
	4	1246	7	2.28			
2	1	1250	7	2.29	2.44	0.19	7.60
	2	1317	7	2.40			
	3	1492	7	2.71			
	4	1290	7	2.35			
3	1	1278	7	2.33	2.15	0.16	7.35
	2	1058	6.983	1.95			
	3	1199	7	2.20			
	4	1164	7	2.14			
4	1	1165	7	2.14	2.20	0.09	4.23
	2	1241	7	2.27			

Sample 2 excluded from rate constant calculations because did not receive full volume of something

Table 7.111. Part II - Replicate 2, Run 2 E1 Results: pH 4, $O_3/H_2O_2 = 4:1$

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	3244	11.65	3.02	3.02	0.01	0.25
	2	3241	11.683	3.02			
	3	3253	11.7	3.03			
	4	3262	11.683	3.03			
1	1	372	11.7	0.72	0.76	0.04	4.72
	2	400	11.65	0.75			
	3	462	11.65	0.79			
	4	461	11.683	0.79			
2	1	828	11.717	1.09	1.35	0.19	14.33
	2	1127	11.667	1.33			
	3	1383	11.7	1.53			
	4	1279	11.717	1.45			
3	1	2043	11.683	2.06	2.23	0.18	8.10
	2	2084	11.683	2.09			
	3	2462	11.7	2.39			
	4	2445	11.683	2.38			
4	1	2525	11.817	2.44	2.45	0.01	0.23
	2	2535	11.683	2.45			

Sample 2 excluded from rate constant calculations because did not receive full volume of something

Table 7.112. Part II - Replicate 2, Run 3 Acetophenone Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	1324	6.933	2.41	2.44	0.04	1.63
	2	1261	6.933	2.30			
	3	1366	6.933	2.49			
	4	1329	6.917	2.42			
1	1	1298	6.917	2.37	2.24	0.14	6.41
	2	1113	6.933	2.05			
	3	1273	6.933	2.33			
	4	1205	6.933	2.21			
2	1	1025	6.917	1.90	2.18	0.24	11.17
	2	1270	6.933	2.32			
	3	1120	6.933	2.06			
	4	1333	6.933	2.43			
3	1	1187	6.917	2.18	2.27	0.12	5.12
	2	1158	6.917	2.13			
	3	1198	6.917	2.20			
	4	1334	6.917	2.43			
	5	1250	6.933	2.29			

Sample 4 not included because didn't have enough E1 stock.

sketchy peak - split

Table 7.113. Part II - Replicate 2, Run 3 E1 Results: pH 4, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	3538	11.567	3.26	3.26	0.02	0.60
	2	3073	11.517	2.88			
	3	3515	11.533	3.24			
	4	3564	11.533	3.28			
1	1	2175	11.5	2.17	2.24	0.09	3.88
	2	2401	11.567	2.35			
	3	2179	11.533	2.17			
	4	2300	11.55	2.27			
2	1	1690	11.517	1.78	1.94	0.12	6.03
	2	2036	11.55	2.05			
	3	1903	11.533	1.95			
	4	1942	11.55	1.98			
3	1	2310	11.517	2.27	2.40	0.11	4.39
	2	2601	11.683	2.51			
	3	2439	11.55	2.38			
	4	2532	11.533	2.45			
	5	2618	11.533	2.52			

Sample 4 not included because didn't have enough E1 stock.

sketchy peak – split

Table 7.114. Part II - Replicate 2, Run 4 Acetophenone Results: pH 8.5, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	2836	6.933	5.04	5.18	0.20	3.84
	2	2998	6.95	5.32			
1	1	2894	6.933	5.14	4.58	0.40	8.72
	2	2438	6.95	4.35			
	3	2379	6.95	4.24			
	4	2584	6.933	4.60			
2	[redacted]				4.59	0.10	2.22
	2	2513	6.95	4.48			
	3	2629	6.933	4.68			
	4	2588	6.933	4.61			
3	1	3052	6.933	5.41	5.13	0.28	5.46
	2	2684	6.95	4.77			
	3	2853	6.933	5.07			
	4	2981	6.95	5.29			
4	1	3079	6.933	5.46	5.47	0.01	0.22
	2	3089	6.933	5.47			

[redacted]

Table 7.115. Part II - Replicate 2, Run 4 E1 Results: pH 8.5, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Control	1	5539	11.55	4.86	5.01	0.22	4.42
	2	5931	11.55	5.17			
1	1	3635	11.533	3.33	3.30	0.03	1.04
	2	3571	11.55	3.28			
	3	3550	11.567	3.26			
	4	3631	11.55	3.33			
2	1	4283	11.533	3.85	3.50	0.11	3.18
	2	3809	11.55	3.47			
	3	3997	11.55	3.62			
	4	3725	11.55	3.40			
3	1	4698	11.533	4.18	4.05	0.15	3.77
	2	4321	11.55	3.88			
	3	4430	11.55	3.97			
	4	4696	11.55	4.18			
4	1	5301	11.55	4.67	4.67	0.01	0.11
	2	5310	11.55	4.67			

Replicate identified as outlier, using Q-test

Table 7.116. Part II - Replicate 2, Run 5 Results: pH 7, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (µM)	Average (µM)	Standard Deviation (µM)	% Difference
Acetophenone							
Control	1 2	3026 3162	6.933 6.95	5.37 5.60	5.48	0.17	3.04
1	1 2	2571 2639	6.95 6.933	4.58 4.69	4.64	0.08	1.80
2	1 2	2689 2726	6.95 6.95	4.78 4.85	4.81	0.05	0.94
3	1 2	2642 2688	6.933 6.933	4.70 4.78	4.74	0.06	1.19
4	1 2	2908 2885	6.933 6.95	5.16 5.12	5.14	0.03	0.55
E1							
Control	1 2	5698 6003	11.55 11.567	4.98 5.23	5.11	0.17	3.38
1	1 2	3766 3991	11.567 11.55	3.44 3.62	3.53	0.13	3.61
2	1 2	4051 3998	11.583 11.583	3.67 3.62	3.64	0.03	0.82
3	1 2	4326 4328	11.55 11.55	3.89 3.89	3.89	0.00	0.03
4	1 2	5091 5034	11.567 11.583	4.50 4.45	4.47	0.03	0.72

Table 7.117. Part II - Replicate 2, Run 6 Results: pH 7, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Acetophenone							
Control	1	2883	6.967	5.12	5.14	0.36	6.92
	2	2622	6.967	4.66			
	3	3113	6.967	5.52			
	4	2955	6.967	5.24			
1	1	2563	6.983	4.56	4.57	0.01	0.27
	2	2573	6.983	4.58			
2	1	2625	6.967	4.67	4.66	0.02	0.34
	2	2612	6.967	4.65			
3	1	2638	6.967	4.69	4.77	0.12	2.41
	2	2732	6.967	4.86			
4	[redacted]				5.07	0.01	0.22
	2	2858	6.967	5.07			
	3	2849	6.983	5.06			
E1							
Control	1	5120	11.65	4.52	4.59	0.19	4.14
	2	4920	11.65	4.36			
	3	5462	11.65	4.79			
	4	5328	11.65	4.69			
1	1	3552	11.65	3.27	3.19	0.10	3.17
	2	3373	11.65	3.12			
2	1	3954	11.65	3.59	3.58	0.02	0.43
	2	3927	11.65	3.57			
3	1	4289	11.65	3.86	3.86	0.01	0.16
	2	4300	11.65	3.86			
4	1	4632	11.633	4.13	4.43	0.12	2.69
	2	4905	11.65	4.35			
	3	5116	11.65	4.52			

[redacted]

Replicate identified as outlier, using Q-test

Table 7.118. Part II - Replicate 2, Run 7 Acetophenone Results: pH 4, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	2931	7.067	5.20	5.19	0.14	2.73
	2	3367	7.067	5.96			
	3	3005	7.067	5.33			
	4	2842	7.083	5.05			
1	1	3005	7.067	5.33	5.17	0.22	4.18
	2	2845	7.083	5.05			
	3	2974	7.05	5.28			
	4	2731	7.05	4.85			
	5	3024	7.05	5.36			
2	1	2858	7.067	5.07	4.91	0.18	3.68
	2	2884	7.083	5.12			
	3	2744	7.05	4.88			
	4	2684	7.05	4.77			
	5	2648	7.05	4.71			
3	1	2963	7.05	5.26	5.00	0.23	4.62
	2	2652	7.083	4.72			
	3	2871	7.067	5.10			
	4	2774	7.1	4.93			
4	1	2989	7.067	5.30	5.00	0.40	8.07
	2	2635	7.067	4.69			
	3	3039	7.067	5.39			
	4	2593	7.1	4.61			

Replicate identified as outlier, using Q-test

Table 7.119. Part II - Replicate 2, Run 7 E1 Results: pH 4, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	5418	11.917	4.76	4.80	0.08	1.57
	[redacted]						
	3	5584	11.95	4.89			
	4	5424	11.917	4.76			
1	1	3161	11.9	2.95	2.83	0.12	4.31
	2	2945	11.917	2.78			
	3	3085	11.75	2.89			
	4	2777	11.75	2.65			
	5	3090	11.75	2.90			
2	1	3392	11.883	3.14	3.07	0.13	4.15
	2	3452	11.933	3.19			
	3	3344	11.75	3.10			
	4	3040	11.767	2.86			
	5	3284	11.767	3.05			
3	1	4236	11.867	3.81	3.60	0.16	4.53
	2	3915	11.917	3.56			
	3	3966	11.917	3.60			
	4	3745	11.933	3.42			
4	1	4938	11.917	4.38	4.20	0.22	5.14
	2	4450	11.9	3.98			
	3	4962	11.933	4.39			
	4	4522	11.933	4.04			

[redacted]

Table 7:120. Part II - Replicate 2, Run 7.2 Acetophenone Results: pH 4, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	2666	7.167	4.74	5.08	0.00	0.07
	2	2864	7.167	5.08			
	3	2861	7.167	5.08			
1	1	2856	7.15	5.07	4.81	0.13	2.78
	2	2763	7.167	4.91			
	3	2654	7.167	4.72			
2	1	2700	7.15	4.80	4.86	0.12	2.39
	2	2910	7.167	5.16			
	3	2694	7.167	4.79			
	4	2813	7.167	5.00			
3	1	2632	7.167	4.68	4.98	0.23	4.52
	2	2870	7.167	5.09			
	3	2931	7.167	5.20			
	4	2783	7.167	4.94			
4	1	2815	7.15	5.00	5.01	0.02	0.42
	2	2832	7.167	5.03			

sketchy - may not include

Table 7.121. Part II - Replicate 2, Run 7.2 E1 Results: pH 4, O_3/H_2O_2 = 2:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	6130	12.3	5.33	5.08	0.00	0.06
	2	5812	12.283	5.07			
	3	5817	12.283	5.08			
1	1	3038	12.3	2.86	2.99	0.08	2.56
	2	3268	12.283	3.04			
	3	3133	12.333	2.93			
2	1	3675	12.283	3.36	3.44	0.07	2.11
	2	3168	12.25	2.96			
	3	3777	12.283	3.45			
	4	3856	12.283	3.51			
3	1	4394	12.267	3.94	4.20	0.19	4.48
	2	4851	12.283	4.31			
	3	4927	12.3	4.37			
	4	4711	12.283	4.19			
4	1	4694	12.283	4.18	4.25	0.10	2.33
	2	4869	12.283	4.32			

sketchy - may not include

Table 7.122. Part II - Replicate 2, Run 8 Acetophenone Results: pH 8.5, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	2960	7.05	5.25	5.08	0.18	3.58
	2	2752	7.067	4.89			
	3	2880	7.067	5.11			
1	1	2801	7.05	4.98	5.05	0.06	1.29
	[redacted]						
	3	2874	7.067	5.10			
	4	2852	7.067	5.06			
2	1	2701	7.05	4.80	4.84	0.05	1.04
	2	2742	7.05	4.87			
3	1	2556	7.05	4.55	4.99	0.32	6.40
	2	2801	7.067	4.98			
	3	2967	7.067	5.26			
	4	2922	7.067	5.18			
4	1	2562	7.05	4.56	5.16	0.45	8.79
	2	2863	7.05	5.08			
	3	3159	7.067	5.60			
	4	3051	7.067	5.41			

[redacted]

Table 7.123. Part II - Replicate 2, Run 8 E1 Results: pH 8.5, O_3/H_2O_2 = 1:2

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Control	1	5656	11.767	4.95	4.79	0.16	3.32
	2	5258	11.8	4.63			
	3	5468	11.767	4.80			
1	1	4214	11.767	3.80	3.97	0.16	4.07
	2	3772	11.767	3.44			
	3	4609	11.783	4.11			
	4	4487	11.783	4.01			
2	1	3946	11.783	3.58	3.58	0.01	0.22
	2	3932	11.767	3.57			
3	1	4113	11.783	3.72	4.14	0.30	7.12
	2	4704	11.8	4.19			
	3	4902	11.8	4.35			
	4	4882	11.75	4.33			
4	1	4697	11.767	4.18	4.46	0.22	4.99
	2	4930	11.783	4.37			
	3	5293	11.783	4.66			
	4	5235	11.75	4.61			

Replicate identified as outlier, using Q-test

Table 7.124. Part II - Replicate 2, Run 9 E1 Results: pH 8.5, O_3/H_2O_2 = 4:1

Sample	HPLC Replicate	PAC	Retention Time (min.)	Concentration (μM)	Average (μM)	Standard Deviation (μM)	% Difference
Acetophenone							
Control	1 2	2913 2896	7.167 7.167	5.17 5.14	5.15	0.02	0.40
1	1 2	2433 2573	7.183 7.167	4.34 4.58	4.46	0.17	3.85
2	1 2 3 4	2401 2525 2807 2888	7.183 7.183 7.183 7.167	4.28 4.50 4.99 5.13	4.72	0.40	8.45
3	1 2 3	2617 2895 2754	7.183 7.183 7.183	4.66 5.14 4.89	4.90	0.24	4.92
4	1 2 3 4	2507 3259 2796 2993	7.167 7.183 7.183 7.167	4.47 5.77 4.97 5.31	5.13	0.55	10.74
E1							
Control	1 2	5401 5593	12.283 12.317	4.75 4.90	4.82	0.11	2.25
1	1 2	3077 3108	12.333 12.3	2.89 2.91	2.90	0.02	0.60
2	1 2 3 4	3998 3659 4170 4157	12.35 12.317 12.317 12.317	3.62 3.35 3.76 3.75	3.62	0.19	5.25
3	1 2 3	4370 4484 4242	12.317 12.333 12.317	3.92 4.01 3.82	3.92	0.10	2.47
4	1 2 3 4	4830 5662 5002 5068	12.317 12.317 12.333 12.317	4.29 4.95 4.43 4.48	4.54	0.29	6.38

Appendix F: Rate constant sample calculations and results, Part II (·OH experiments)

kOH,acetophenone = 5.9×10^9 $M^{-1}s^{-1}$ (Willson et al., 1971).

$$\ln\left(\frac{[M(n)]}{[M(0)]}\right) = \ln\left(\frac{[R(n)]}{[R(0)]}\right)\frac{k_{oxidant}(M)}{k_{oxidant}(R)}$$ (Huber et al., 2003)

y = mx

$$m = \frac{k_{oxidant}(M)}{k_{oxidant}(R)} \rightarrow k_{oxidant}(M) = m\, k_{oxidant}(R)$$

Table 7.125. Part II - Replicate 1, Run 1 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 2:1

	Acetophenone Concentration (µM)		E1 Concentration (µM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.89	0.27	2.22	0.19
3	1.71	0.37	1.18	0.22
4	1.78	0.12	1.62	0.03
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
3	0.90	-0.10	0.53	-0.63
4	0.94	-0.06	0.73	-0.32

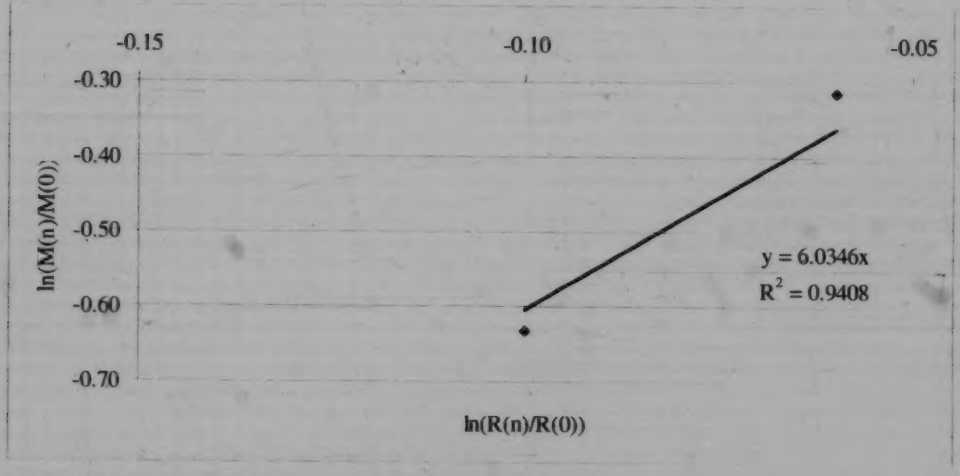

Figure 7.35. Competitive Kinetics ·OH Results, Replicate 1, Run 1: pH 4, O_3/H_2O_2 = 2:1

m =6.0346
$k_{OH\,E1} = 3.56 \times 10^{10}$ $M^{-1}s^{-1}$

Table 7.126. Part II - Replicate 1, Run 1.2 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 2:1

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	5.26	0.26	4.75	0.11
1	5.08	0.22	2.47	0.13
2	5.04	0.08	2.97	0.12
3	5.19	0.19	3.73	0.10
4	5.25	0.28	4.54	0.29
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.97	-0.03	0.52	-0.65
2	0.96	-0.04	0.63	-0.47
3	0.99	-0.01	0.79	-0.24
4	1.00	0.00	0.96	-0.05

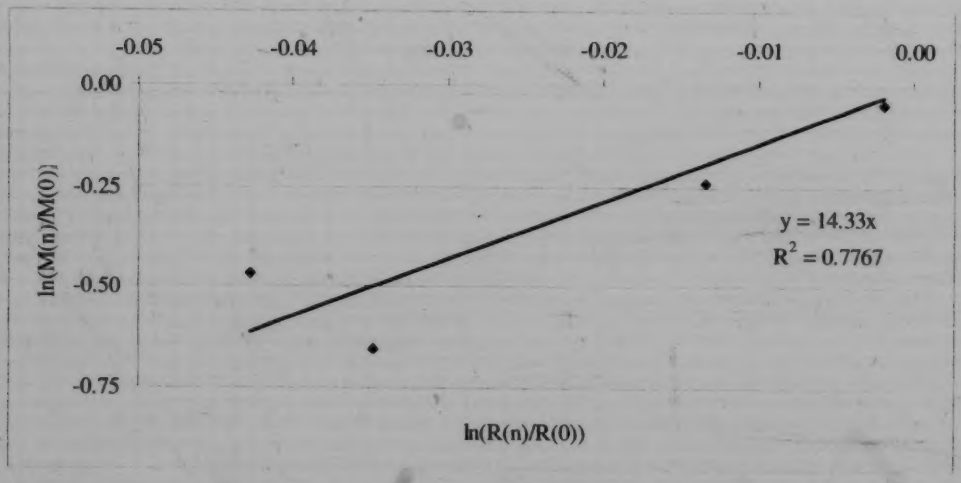

Figure 7.36. Competitive Kinetics ·OH Results, Replicate 1, Run 1.2: pH 4, O_3/H_2O_2 = 2:1

m = 14.33

$k_{OH\,E1} = 8.45 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.127. Part II - Replicate 1, Run 2 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 4:1

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.10	0.05	2.51	0.10
1	1.39	0.01	1.17	0.03
2	1.64	0.31	1.31	0.13
3	1.94	0.07	2.16	0.17
4	2.06	0.14	2.13	0.09
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.66	-0.41	0.46	-0.77
2	0.78	-0.25	0.52	-0.65
3	0.92	-0.08	0.86	-0.15
4	0.98	-0.02	0.85	-0.16

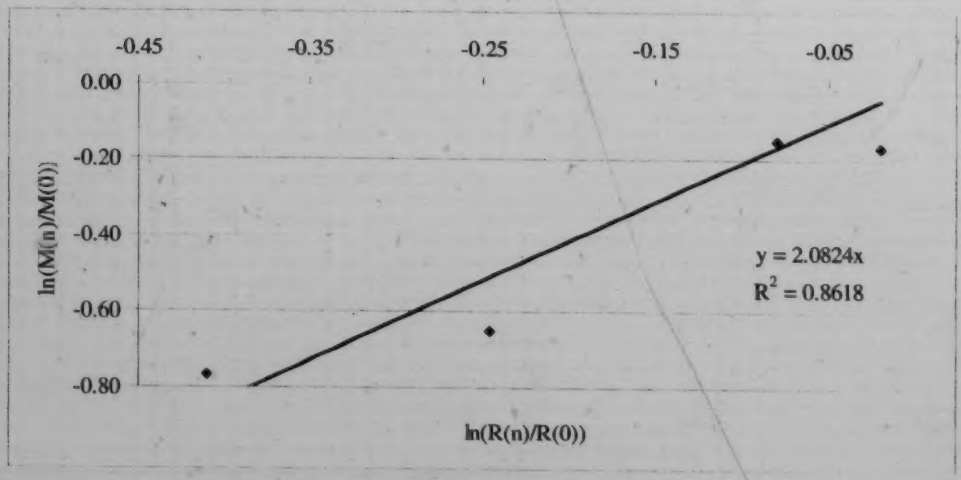

Figure 7.37. Competitive Kinetics ·OH Results, Replicate 1, Run 2: pH 7, O_3/H_2O_2 = 4:1

m = 2.0824
$k_{OH\,E1} = 1.23 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.128. Part II - Replicate 1, Run 3 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 1:2

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.89	0.15	2.40	0.16
1	1.66	0.16	1.43	0.12
2	1.71	0.02	1.63	0.06
3	1.93	0.10	2.03	0.03
4	1.93	0.23	2.22	0.18
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.88	-0.13	0.60	-0.52
2	0.91	-0.10	0.68	-0.39
3	1.02	0.02	0.85	-0.17
4	1.02	0.02	0.93	-0.08

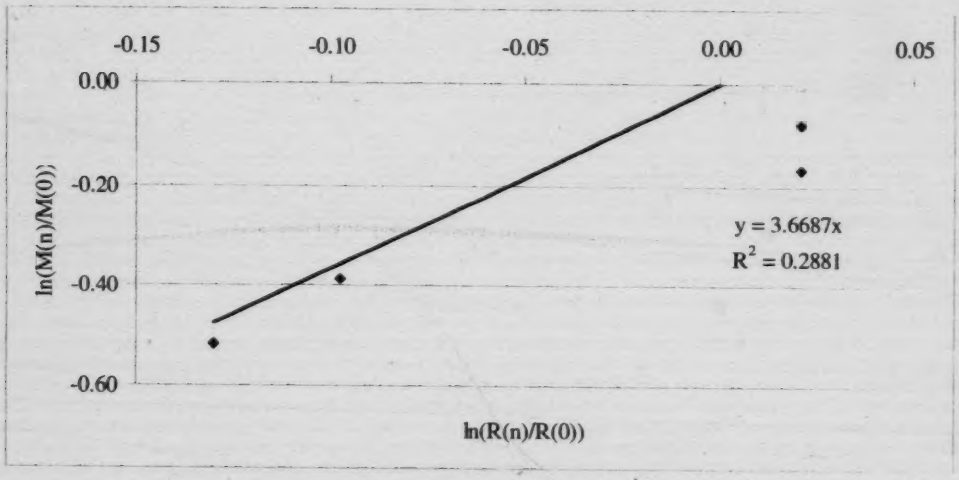

Figure 7.38. Competitive Kinetics ·OH Results, Replicate 1, Run 3: pH 4, O_3/H_2O_2 = 1:2

m = 3.6687
$k_{OH\,E1} = 2.16 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.129. Part II - Replicate 1, Run 4 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 4:1

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	1.59	0.14	2.76	0.22
1	1.22	0.02	1.31	0.08
2	1.24	0.07	1.66	0.17
3	1.31	0.15	2.02	0.19
4	1.45	0.05	2.36	0.04
Sample	R(n)/R(0)	ln(R(n)/R0)	M(n)/M(0)	ln(M(n)/M(0))
1	0.77	-0.26	0.47	-0.75
2	0.78	-0.25	0.60	-0.51
3	0.82	-0.19	0.73	-0.31
4	0.91	-0.09	0.86	-0.16

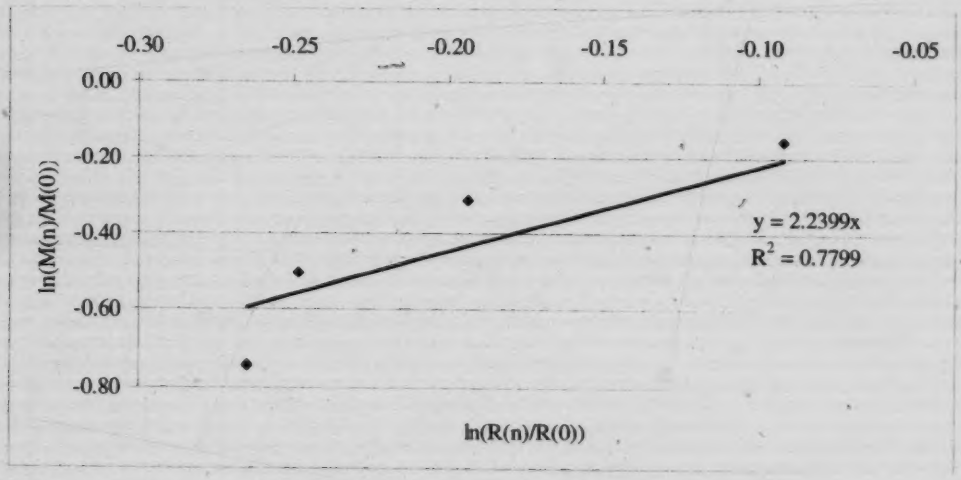

Figure 7.39. Competitive Kinetics ·OH Results, Replicate 1, Run 4: pH 8.5, O_3/H_2O_2 = 4:1

m = 2.2399
$k_{OH\,E1} = 1.32 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.130. Part II - Replicate 1, Run 5 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 4:1

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.51	0.08	3.08	0.01
1	2.13	0.18	0.67	0.04
2	2.28	0.14	1.36	0.04
3	2.24	0.12	1.85	0.26
4	2.45	0.02	3.16	0.09
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.85	-0.16	0.22	-1.53
2	0.91	-0.10	0.44	-0.82
3	0.89	-0.11	0.60	-0.51
4	0.98	-0.02	1.03	0.03

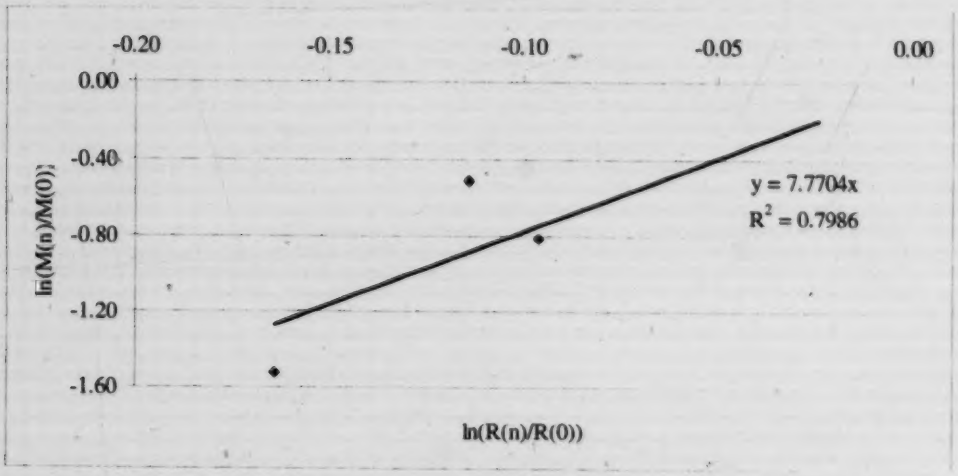

Figure 7.40. Competitive Kinetics ·OH Results, Replicate 1, Run 5: pH 4, O_3/H_2O_2 = 4:1

m = 7.7704
$k_{OH\,E1} = 4.58 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.131. Part II - Replicate 1, Run 6 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 1:2

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.07	0.08	2.80	0.14
1	1.73	0.07	1.91	0.12
2	1.85	0.05	1.93	0.12
3	1.97	0.05	2.28	0.18
4	1.90	0.10	2.58	0.12
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.84	-0.18	0.68	-0.38
2	0.89	-0.11	0.69	-0.37
3	0.95	-0.05	0.81	-0.21
4	0.92	-0.09	0.92	-0.08

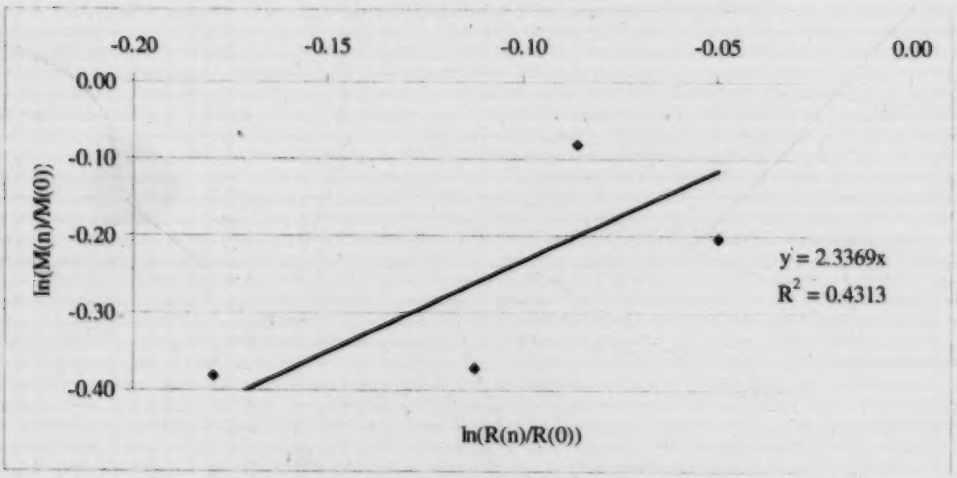

Figure 7.41. Competitive Kinetics ·OH Results, Replicate 1, Run 6: pH 8.5, O_3/H_2O_2 = 1:2

m = 2.3369
$k_{OH\,E1} = 1.38 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.132. Part II - Replicate 1, Run 6.2 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 1:2

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	5.56	0.01	5.13	0.09
1	4.66	0.09	3.75	0.08
2	5.00	0.33	3.92	0.18
3	5.20	0.07	4.01	0.19
4	5.49	0.17	4.73	0.20
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.84	-0.18	0.73	-0.31
2	0.90	-0.11	0.76	-0.27
3	0.94	-0.07	0.78	-0.25
4	0.99	-0.01	0.92	-0.08

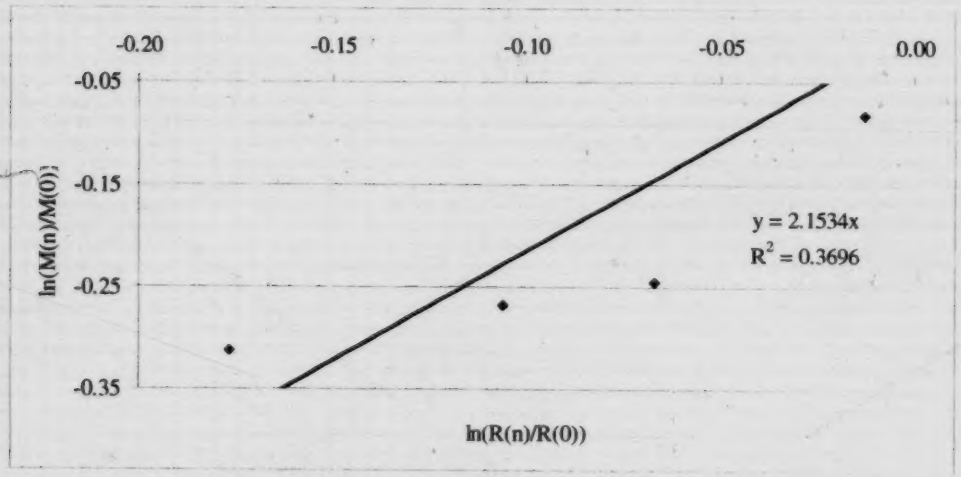

Figure 7.42. Competitive Kinetics ·OH Results, Replicate 1, Run 6.2: pH 8.5, O_3/H_2O_2 = 1:2

m = 2.1534
$k_{OH,E1} = 1.27 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.133. Part II - Replicate 1, Run 7 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 2:1

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.20	0.03	2.87	0.05
1	1.61	0.05	1.31	0.00
2	1.68	0.14	1.54	0.05
3	1.82	0.03	1.88	0.02
4	2.03	0.04	2.37	0.19
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.73	-0.31	0.46	-0.78
2	0.76	-0.27	0.54	-0.62
3	0.83	-0.19	0.66	-0.42
4	0.92	-0.08	0.83	-0.19

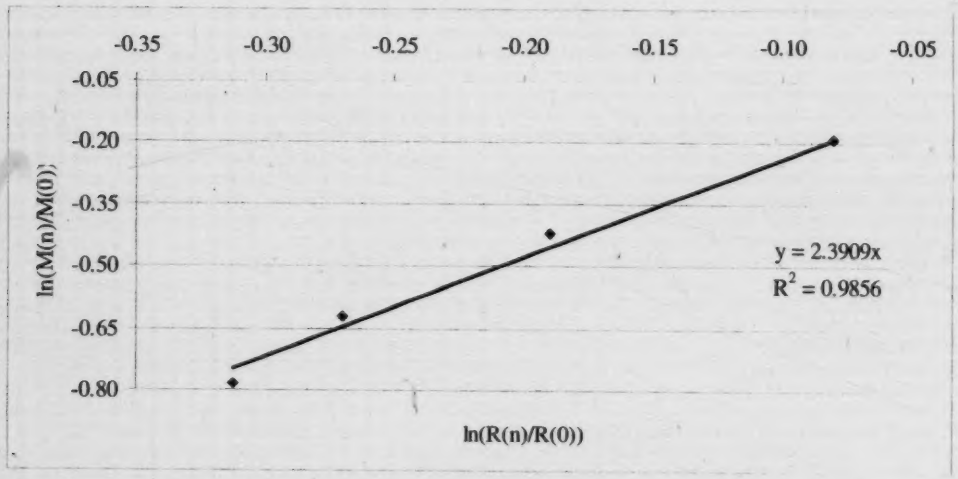

Figure 7.43. Competitive Kinetics ·OH Results, Replicate 1, Run 7: pH 8.5, O_3/H_2O_2 = 2:1

m = 2.3909
$k_{OH\,E1} = 1.41 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.134. Part II - Replicate 1, Run 8 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 2:1

	Acetophenone Concentration (µM)		E1 Concentration (µM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.96	0.02	2.98	0.13
1	2.09	0.03	1.46	0.01
2	2.33	0.09	2.16	0.08
3	2.16	0.06	1.86	0.06
4	2.42	0.05	2.24	0.01
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.71	-0.35	0.49	-0.71
2	0.79	-0.24	0.72	-0.32
3	0.73	-0.32	0.62	-0.47
4	0.82	-0.20	0.75	-0.29

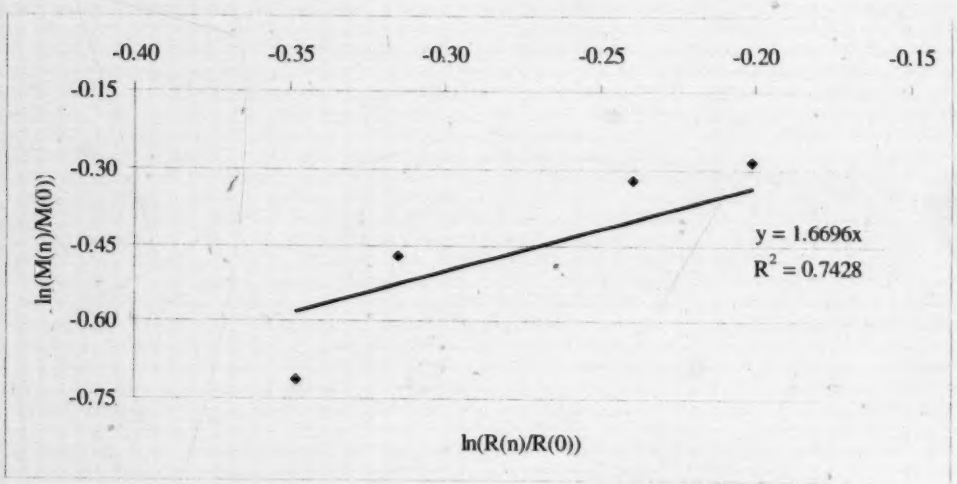

Figure 7.44. Competitive Kinetics ·OH Results, Replicate 1, Run 8: pH 7, O_3/H_2O_2 = 2:1

m = 1.6696
$k_{OH\,E1} = 9.85 \times 10^9\ M^{-1}s^{-1}$

Table 7.135. Part II - Replicate 1, Run 9 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 1:2

	Acetophenone Concentration (µM)		E1 Concentration (µM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.26	0.05	2.83	0.02
1	2.19	0.21	2.14	0.18
2	2.05	0.14	2.04	0.07
3	2.21	0.24	2.22	0.13
4	2.19	0.21	2.61	0.16
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.97	-0.03	0.76	-0.28
2	0.91	-0.10	0.72	-0.33
3	0.98	-0.02	0.78	-0.24
4	0.97	-0.03	0.92	-0.08

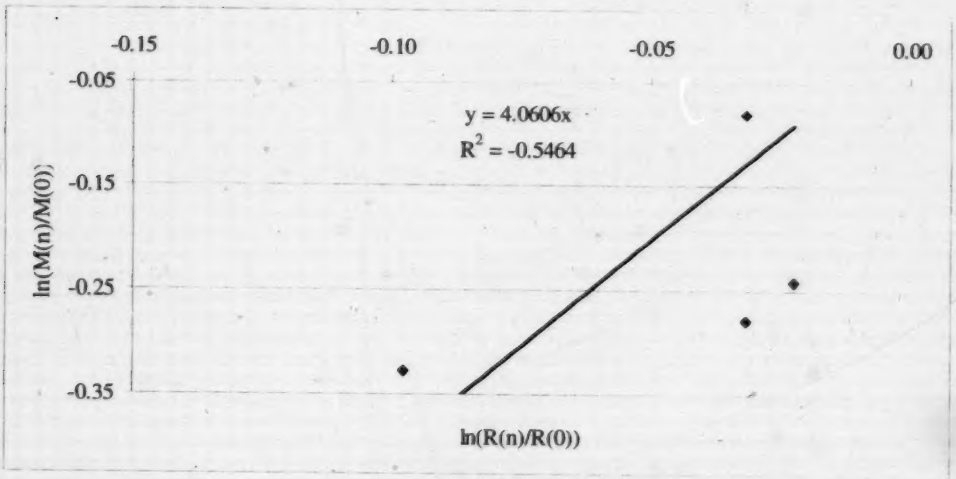

Figure 7.45. Competitive Kinetics ·OH Results, Replicate 1, Run 9: pH 7, O_3/H_2O_2 = 1:2

m = 4.0606
$k_{OH\,E1} = 2.40 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.136. Part II - Replicate 1, Run 9.2 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 1:2

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	5.39	0.07	5.67	0.19
1	5.14	0.19	4.50	0.11
2	5.26	0.19	4.68	0.23
3	5.30	0.17	5.12	0.10
4	5.36	0.34	5.22	0.32
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.95	-0.05	0.79	-0.23
2	0.98	-0.02	0.83	-0.19
3	0.98	-0.02	0.90	-0.10
4	0.99	-0.01	0.92	-0.08

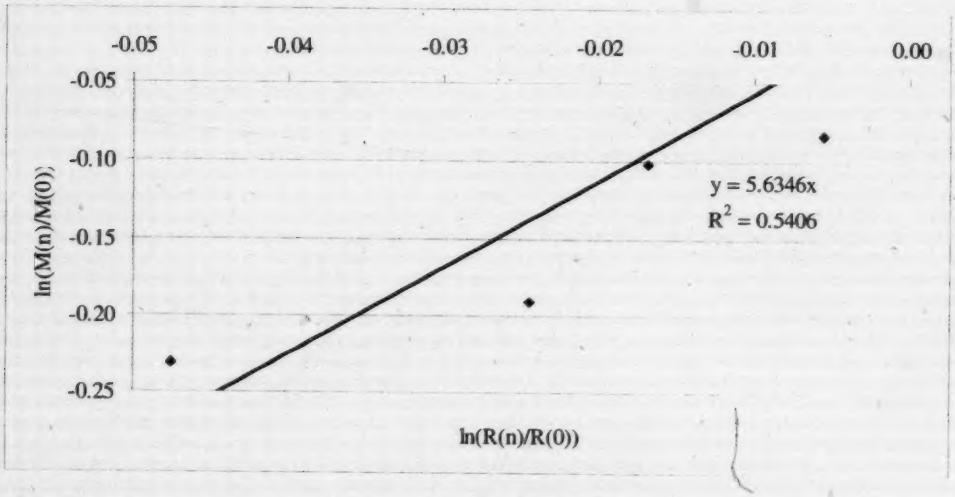

Figure 7.46. Competitive Kinetics ·OH Results, Replicate 1, Run 9.2: pH 7, O_3/H_2O_2 = 1:2

m = 5.6346
$k_{OH\,E1} = 3.32 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.137. Part II - Replicate 2, Run 1 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 1:2

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.48	0.22	2.83	0.16
1	2.08	0.10	1.92	0.03
2	2.19	0.20	2.37	0.12
3	2.23	0.16	2.46	0.03
4	2.16	0.03	2.42	0.02
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.84	-0.18	0.68	-0.39
2	0.88	-0.12	0.84	-0.18
3	0.90	-0.11	0.87	-0.14
4	0.87	-0.14	0.86	-0.16

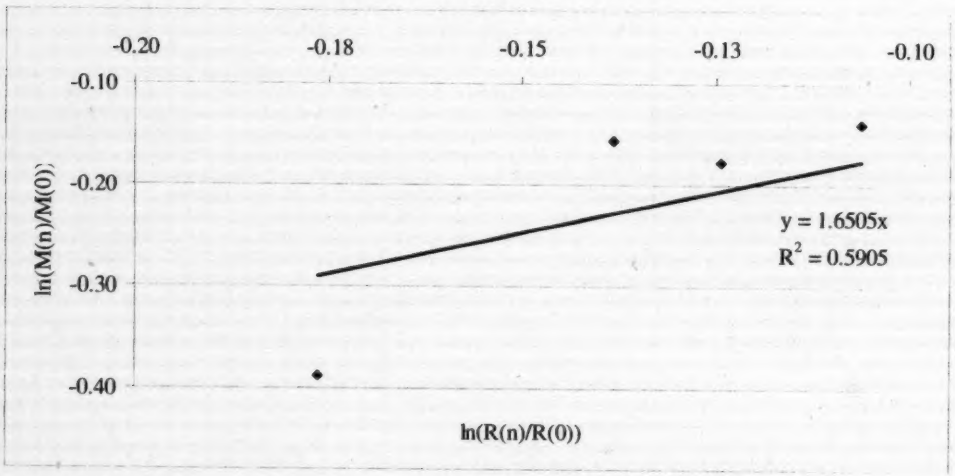

Figure 7.47. Competitive Kinetics ·OH Results, Replicate 2, Run 1: pH 7, O_3/H_2O_2 = 1:2

m = 1.6505
$k_{OH\,E1} = 9.74 \times 10^9\ M^{-1}s^{-1}$

Table 7.138. Part II - Replicate 2, Run 2 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 4:1

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.41	0.12	3.02	0.01
1	2.10	0.18	0.76	0.04
3	2.15	0.16	2.23	0.18
4	2.20	0.09	2.45	0.01
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.87	-0.14	0.25	-1.38
3	0.89	-0.11	0.74	-0.30
4	0.91	-0.09	0.81	-0.21

Sample 2 excluded because did not receive full volume of something

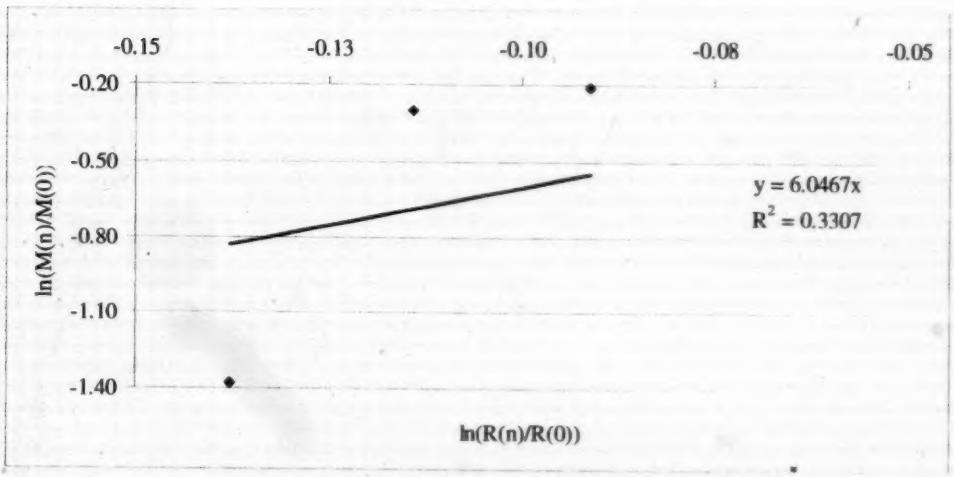

Figure 7.48. Competitive Kinetics ·OH Results, Replicate 2, Run 2: pH 4, O_3/H_2O_2 = 4:1

m = 6.0467

$k_{OH\,E1} = 3.57 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.139. Part II - Replicate 2, Run 3 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 1:2

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	2.44	0.04	3.26	0.02
1	2.24	0.14	2.24	0.09
2	2.18	0.24	1.94	0.12
3	2.27	0.12	2.40	0.11
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.92	-0.09	0.69	-0.38
2	0.89	-0.11	0.60	-0.52
3	0.93	-0.07	0.74	-0.31

Sample 4 not included because didn't have enough E1 stock.

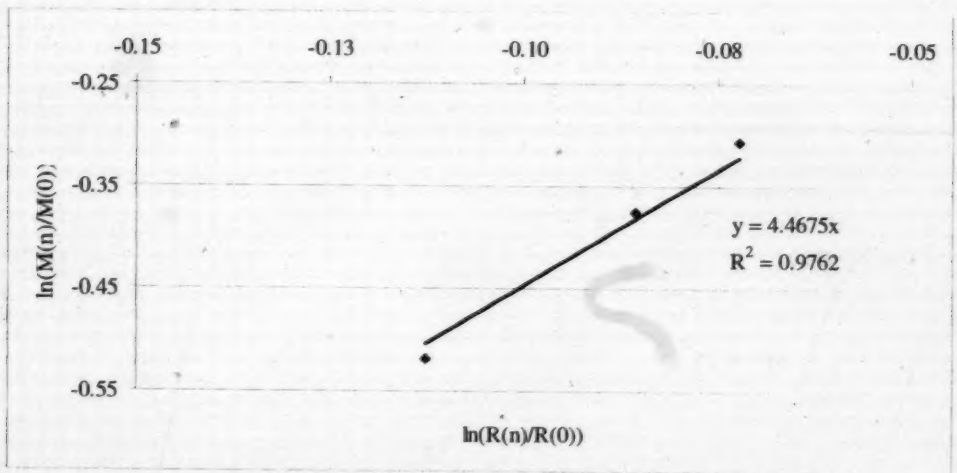

Figure 7.49. Competitive Kinetics ·OH Results, Replicate 2, Run 3: pH 4, O_3/H_2O_2 = 1:2

m = 4.4675
$k_{OH\,E1} = 2.64 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.140. Part II - Replicate 2, Run 4 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 2:1

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	5.18	0.20	5.01	0.22
1	4.58	0.40	3.30	0.03
2	4.59	0.10	3.50	0.11
3	5.13	0.28	4.05	0.15
4	5.47	0.01	4.67	0.01
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.88	-0.12	0.66	-0.42
2	0.89	-0.12	0.70	-0.36
3	0.99	-0.01	0.81	-0.21
4	1.06	0.05	0.93	-0.07

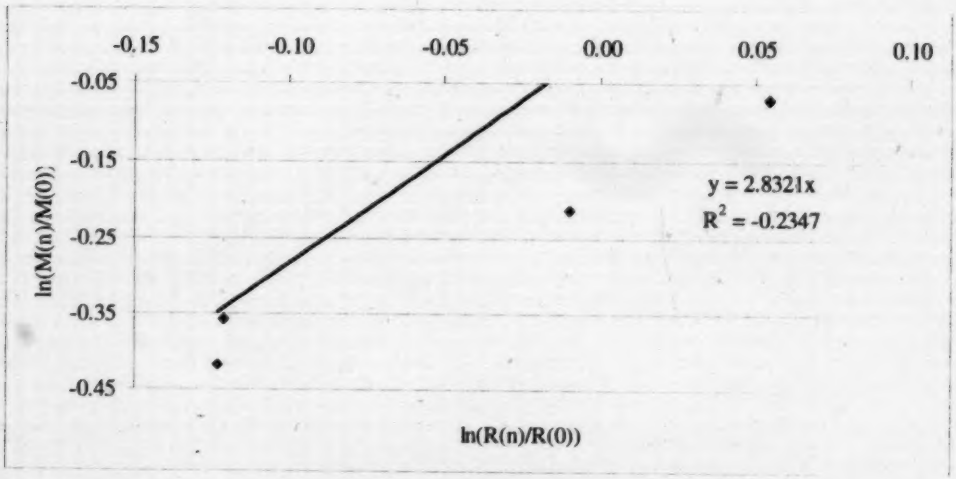

Figure 7.50. Competitive Kinetics ·OH Results, Replicate 2, Run 4: pH 8.5, O_3/H_2O_2 = 2:1

m = 2.8321
$k_{OH\,E1} = 1.67 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.141. Part II - Replicate 2, Run 5 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 2:1

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	5.48	0.17	5.11	0.17
1	4.64	0.08	3.53	0.13
2	4.81	0.05	3.64	0.03
3	4.74	0.06	3.89	0.00
4	5.14	0.03	4.47	0.03
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.85	-0.17	0.69	-0.37
2	0.88	-0.13	0.71	-0.34
3	0.86	-0.15	0.76	-0.27
4	0.94	-0.06	0.88	-0.13

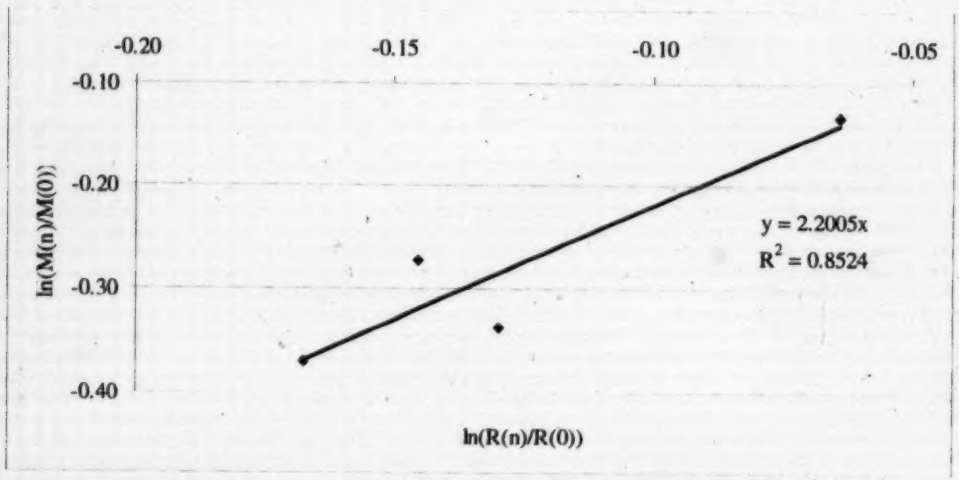

Figure 7.51. Competitive Kinetics ·OH Results, Replicate 2, Run 5: pH 7, O_3/H_2O_2 = 2:1

m = 2.2005
$k_{OH\,E1} = 1.3 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.142. Part II - Replicate 2, Run 6 Rate Constant Calculations: pH 7, O_3/H_2O_2 = 4:1

	Acetophenone Concentration (µM)		E1 Concentration (µM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	5.14	0.36	4.59	0.19
1	4.57	0.05	3.19	0.10
2	4.66	0.02	3.58	0.02
3	4.77	0.12	3.86	0.01
4	5.07	0.01	4.43	0.12
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.89	-0.12	0.70	-0.36
2	0.91	-0.10	0.78	-0.25
3	0.93	-0.07	0.84	-0.17
4	0.99	-0.01	0.97	-0.04

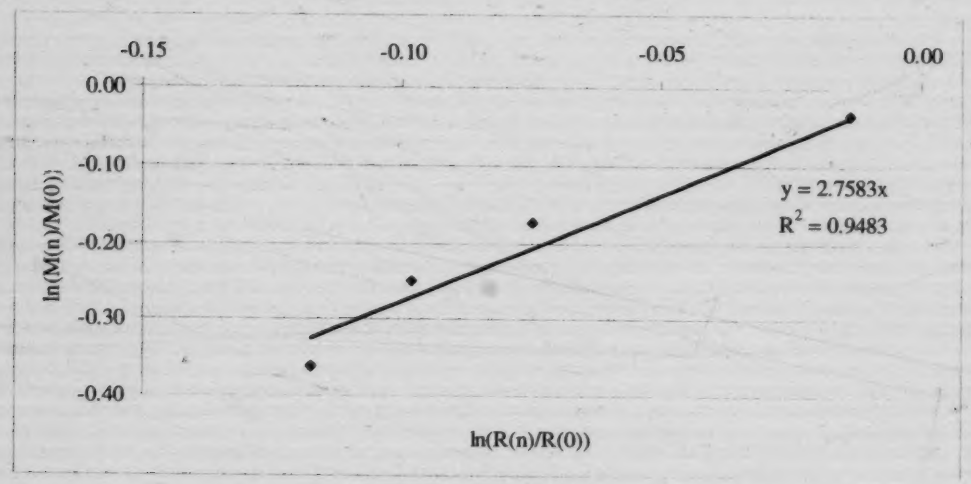

Figure 7.52. Competitive Kinetics ·OH Results, Replicate 2, Run 6: pH 7, O_3/H_2O_2 = 4:1

m = 2.7583
$k_{OH\,E1} = 1.63 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.143. Part II - Replicate 2, Run 7 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 2:1

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	5.19	0.14	4.80	0.08
1	5.17	0.22	2.83	0.12
2	4.91	0.18	3.07	0.13
3	5.00	0.23	3.60	0.16
4	5.00	0.40	4.20	0.22

Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	1.00	0.00	0.59	-0.53
2	0.95	-0.06	0.64	-0.45
3	0.96	-0.04	0.75	-0.29
4	0.96	-0.04	0.88	-0.13

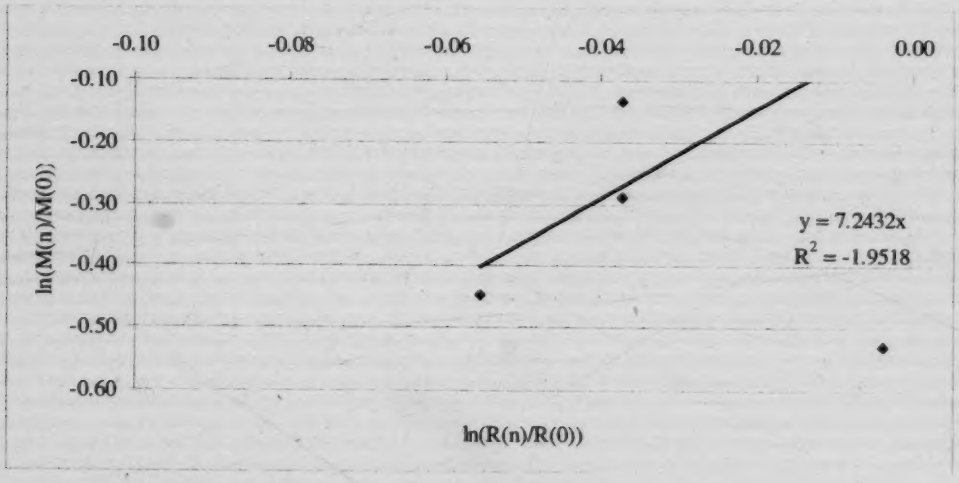

Figure 7.53. Competitive Kinetics ·OH Results, Replicate 2, Run 7: pH 4, O_3/H_2O_2 = 2:1

m = 7.2432
$k_{OH\,E1} = 4.27 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.144. Part II - Replicate 2, Run 7.2 Rate Constant Calculations: pH 4, O_3/H_2O_2 = 2:1

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	5.08	0.00	5.08	0.00
1	4.81	0.13	2.99	0.08
2	4.86	0.12	3.44	0.07
3	4.98	0.23	4.20	0.19
4	5.01	0.02	4.25	0.10
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.95	-0.05	0.59	-0.53
2	0.96	-0.04	0.68	-0.39
3	0.98	-0.02	0.83	-0.19
4	0.99	-0.01	0.84	-0.18

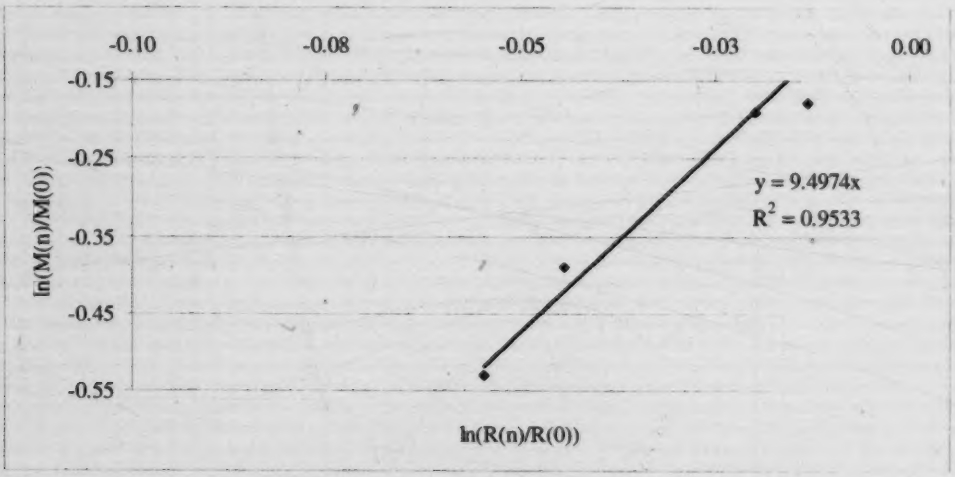

Figure 7.54. Competitive Kinetics ·OH Results, Replicate 7.2, Run 2: pH 4, O_3/H_2O_2 = 2:1

m = 9.4974
$k_{OH\,E1} = 5.6 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.145. Part II - Replicate 2, Run 8 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 1:2

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	5.08	0.18	4.79	0.16
1	5.05	0.06	3.97	0.16
2	4.84	0.05	3.58	0.01
3	4.99	0.32	4.14	0.30
4	5.16	0.45	4.46	0.22
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.99	-0.01	0.83	-0.19
2	0.95	-0.05	0.75	-0.29
3	0.98	-0.02	0.86	-0.15
4	1.02	0.02	0.93	-0.07

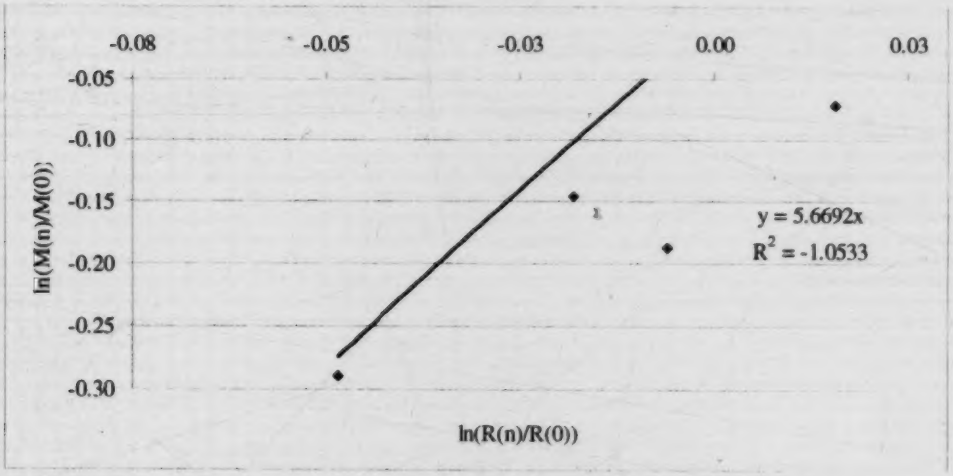

Figure 7.55. Competitive Kinetics ·OH Results, Replicate 2, Run 8: pH 8.5, O_3/H_2O_2 = 1:2

m = 5.6692
$k_{OH\,E1} = 3.34 \times 10^{10}\ M^{-1}s^{-1}$

Table 7.146. Part II - Replicate 2, Run 9 Rate Constant Calculations: pH 8.5, O_3/H_2O_2 = 4:1

	Acetophenone Concentration (μM)		E1 Concentration (μM)	
Sample	Average	Standard Deviation	Average	Standard Deviation
Control	5.15	0.02	4.82	0.11
1	4.46	0.17	2.90	0.02
2	4.72	0.40	3.62	0.19
3	4.90	0.24	3.92	0.10
4	5.13	0.55	4.54	0.29
Sample	R(n)/R(0)	ln(R(n)/R(0))	M(n)/M(0)	ln(M(n)/M(0))
1	0.87	-0.14	0.60	-0.51
2	0.92	-0.09	0.75	-0.29
3	0.95	-0.05	0.81	-0.21
4	1.00	0.00	0.94	-0.06

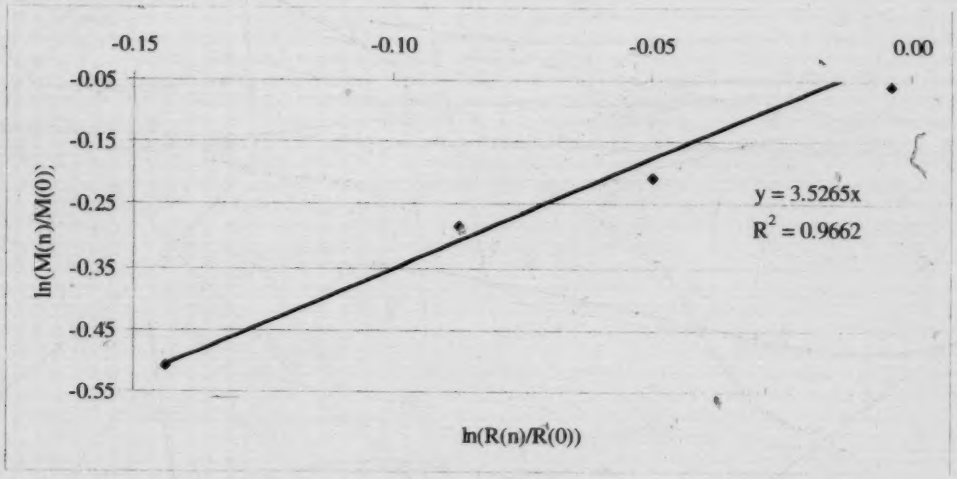

Figure 7.56. Competitive Kinetics ·OH Results, Replicate 2, Run 9: pH 8.5, O_3/H_2O_2 = 4:1

m = 3.5265
$k_{OH\,E1} = 2.08 \times 10^{10}\ M^{-1}s^{-1}$